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<b>(54) Title:</b> CONTROLLED RELEASE COMPOSITION OF BIOCIDES IN AN AQUEOUS DISPERSION OF VISCOUS OIL  <b>(57) Abstract</b>  Controlled release composition (dispersion) characterised by its non active ingredient which is a viscous oil selected from the group consisting of bitumen, abietic acid, ester derivatives of abietic acid, carboxylic acid containing materials and carboxylic acid ester containing materials. (Also disclosed are methods of preparation and use of composition).		

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## Controlled release composition of biocide in an aqueous dispersion of viscous oil

### FIELD OF THE INVENTION

This invention relates to improved controlled release compositions that allow an active ingredient to be released in a controlled manner, and in particular to such compositions that are in the form of aqueous dispersions. The invention also relates to methods of preparing controlled release compositions in the form of an aqueous dispersion.

### BACKGROUND OF THE INVENTION

Controlled release formulations in the form of aqueous emulsions have been previously disclosed in PCT/AU 89/00230.

There are several ways in which the use of such types of controlled release formulations in the form of aqueous dispersions can be of increased benefit relative to known compositions of active.

1. The controlled release formulation may decrease the rate of release of active ingredient from the formulation, leading to a longer period of efficacy or, if the active is volatile, leading to reduced loss of active to the atmosphere.
2. The controlled release formulation may be safer to handle and store.
3. The controlled release formulation may contain less volatile solvent.
4. The controlled release formulation may be less harmful to beneficial species. For example, a controlled release cereal herbicide may be less damaging to germinating wheat than a standard formulation such as an emulsion concentrate.
5. The controlled release formulation may enhance the potency of the active ingredient, for example by improving the uniformity of distribution of the active ingredient in soil.

SUMMARY OF PRIOR ART

Previous aqueous dispersions for the controlled release of active ingredients have included the following types:

- 5 a. Dispersions where a chemical reaction occurs after the formation of the dispersion, creating a solid matrix from an originally liquid disperse phase. Examples include the formulation of poly-urea capsules and the formation of a polymer matrix from liquid monomers by polymerisation. Specific examples are disclosed in Australian Patent Application No. 37393/85 and U.S. Patent No. 3,212,967.
- 10 b. Dispersions where an organic solvent is removed from the disperse phase after the formation of the dispersion, leaving a solid disperse mass as host matrix, for example the formation of polylactide micro-capsules. An example is disclosed in Japanese Patent Application No. 48923/85.
- 15 c. Dispersions in which a solid coating is formed on the outer boundary of the disperse phase by the process of polymer coacervation (i.e. controlled precipitation of polymers at the interface). An example is disclosed in British Patent No. 929405.
- 20 d. Dispersions in which the matrix is heated to elevated temperatures prior to the addition of the active ingredient or ingredients, and in which the molten mass is added with vigorous stirring to an aqueous phase in the presence of surfactants to form a stable emulsion.

This last type of dispersion has been alleged to be useful in the following cases:

- (i) Composition for the protection of wood using a dispersion of fungicide and insecticide in an oily matrix (Pojurowski French Patent Publication No. 2,392,787).
- 25 (ii) Composition with improved biocidal properties using a dispersion e.g. of pentachlorophenol in paraffin (Mobil Australian Patent Application No. 19222/70). In this instance, it was observed that the dispersions were also useful for imparting water resistant properties to treated surfaces (e.g. wood).

30 Using these compositions, the delivery of active ingredient at the site of application of the composition may occur at a reduced rate when compared with the performance of standard

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compositions of the same active substance.

5 In many cases it is important to decrease the rate of release of active ingredient from the controlled release formulation relative to the rate of release of active from the standard formulation by a considerable amount before significant product advantages can be obtained. This advantage is usually sought in terms of increased efficacy of the controlled release formulation. See for example, the publication of Marvin M. Schreiber et al in "Weed Science" Vol 35 No. 3 pages 407-II (1987).

10 The required reduction of release rate in the controlled release product depends on both the nature of the active ingredient and on the performance of the standard formulation of the active material.

15 It is an object of the present invention to provide improved controlled release compositions and in particular controlled release formulations of dinitroaniline herbicides, chloroacetanilide herbicides and organophosphate insecticides, preferably trifluralin, metolachlor and chlorpyrifos where the formulations show decreased volatile loss of active ingredient and/or reduced phytotoxicity to crops in field applicants and/or increased or equal efficacy.

The invention also relates to methods of preparing controlled release compositions in the form of aqueous dispersions.

20 The term "viscous oil" is defined for the purposes of this invention as any naturally occurring hydrocarbon crude oil or any residual oil remaining after refining operations which is generally characterised by a viscosity of about  $10^2$  -  $10^6$  centipoise or greater and otherwise generally, but not necessarily, characterised by an API gravity of about 20°API or less, high metal content, high sulfur content, high asphaltene content and/or high pour point. The term "viscous oil" it is to be understood also to encompass the following: vacuum residuals, 25 vis-breaker residuals, catalytic-cracker residuals, catalytic hydrogenated residuals, coker residuals, ROSE (residual oil supercritical extraction) residuals, tars and cut-back tars, bitumen, pitch and any other terms describing residuals of hydrocarbon processing. The term "viscous oil" encompasses naturally occurring viscous crude oils (also called heavy crude oils) as well as residual bottom-of-the-barrel products from refineries, such as vacuum 30 residues and other residual fuel oils and asphalt. While low gravity does not necessarily coincide with high density, these characteristics are generally correlated in viscous hydrocarbons.

Generally the following characteristics are considered typical of the types of crude oils and residual oils which are useful for the present invention.

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1. Low API gravity, generally at or below 20°API. This is the most frequently used criterion, both because it is easily measured and because 20°API crude roughly corresponds to the lower limit recoverable with conventional production techniques.
- 5 2. Viscosities in the range of about  $10^2$  to  $10^6$  centipoise (cp) or even higher in some cases. For those materials that are solids at ambient temperatures it is a requirement that they have a viscosity of at least 100 centipoise at 120°C.
3. High metal contents. For example, heavy crudes often have nickel and vanadium contents as high as 500 ppm.
- 10 4. High sulfur content, eg, 3 weight percent or more.
5. High asphaltene content.
6. High pour point.

15 The "viscous oils" can be generally defined as having a paraffin content of about 50% by weight or less and an aromatic content of about 15% by weight or greater with viscosities of about 100 centipoise or greater at 65°. The viscous residuals generally are characterised by a paraffin content in the range from about 4% to about 40% by weight, an aromatic content in the range from about 15% to about 70% by weight and an asphaltene content from about 5% to about 80% by weight.

20 In addition, the term "viscous oil" includes heads and bottoms of crude tall oil (a wood derivative) abietic acid, especially as wood rosin and chemical derivatives of abietic acid eg, the maleic anhydride adduct of abietic acid and especially chemical derivatives of abietic acid which exhibit ester functionality, eg the condensation product of abietic acid, maleic anhydride and glycerol. Other polyhydric alcohols may also be used, though glycerol is preferred. Other viscous hydrocarbons suitable for this invention are the bottoms of any  
25 distillation column of processes used to extract natural oils eg, eucalyptus oil.

In addition, the term "viscous oil" includes substances which are solid at room temperature but become viscous oils as described herein in the range 20-120°C.

30 Preferably the "viscous oil" is selected from heads and bottoms of crude tall oil, distillation bottoms of oil extraction processes (oil of mineral natural, vegetable or animal origin), wood rosin, and derivatives of wood rosin. More preferably the "viscous oil" is selected from

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bitumen, wood rosin, derivatives of wood rosin with ester functionality and mixtures of above. The "viscous oil" may also be selected from materials having carboxylic acid groups or carboxylic acid ester groups such as maleic ester residues.

5       Stabilising amounts of surfactants are present in compositions of our invention. Combinations of surfactant types such as non-ionic and anionic are particularly useful. Preferred ionic surfactants are: calcium dodecyl benzene sulphonate (linear or branched chain), metal and amine salts of organic acids (eg, stearic, oleic and abietic acid) amine ethoxylates and primary, secondary and tertiary alkylamines.

10       Preferred non-ionic surfactants are amine ethoxylates and alkylphenol ethoxylates and ethoxylates and propoxylates of polyhydric alcohols such as sorbitol and glycerol. Other preferred surfactants are copolymers of polyoxyethylene and polyoxypropylene, and alkyl and alkylphenol adducts of such copolymers.

15       Further preferred surfactants are Vinsol (trademark of Hercules Pty Ltd), alpha oleum sulphonate, alkyl dimethyl benzyl ammonium chloride and cetyl trimethyl ammonium bromide.

Preferably a mixture of ionic and non-ionic surfactants are used and especially preferred are combinations of anionic and non-ionic surfactants.

Any of the surfactants of the formulation may be added to the oil phase or the aqueous phase, or to both.

20       In choosing the appropriate surfactants for the invention, the physical stability of the emulsion was an important criteria. Stability ensures that there is adequate shelf stability for a commercial product.

Stability of emulsions was assessed using the following criteria:

i)       Particle Size

25       Emulsions were diluted, 1% in water and viewed under a microscope. A subjective determination of common particle size range was performed and degree of flocculation was also noted.

ii)      Dispersability in Water

Emulsions were diluted 1% in water and ease of dispersion was assessed by eye.

iii) Appearance and Colour

The colour and appearance of the emulsion was observed immediately after preparation. The colour was used as an initial estimation of particle size. For coloured matrices, a paler appearance was taken to indicate smaller particle size.

5 iv) Bench Stability

Inversion: The resistance of emulsions was measured to ensure emulsions were water external. This was performed with a multimeter using standard procedure.

Phasing: Any gross settling of particles was deemed unacceptable as determined by the eye.

10 Crystallisation: The surface and bulk of emulsions were inspected regularly by eye to note the first signs of crystallization and hence failure to yield a stable emulsion. Results were confirmed by examination of emulsions under an optical microscope using crossed polarising lenses.

15 The following studies used trifluralin as the active material and bitumen as the matrix material. A range of nonionic surfactants including: nonyl phenol ethoxylates, other fatty alcohol ethoxylates, and fatty amine ethoxylates was evaluated in combination with an anionic emulsifier. The ratio of anionic emulsifier (e.g. vinsol resin) and nonionic emulsifier and the HLB of the various nonionic surfactants were investigated over a number of differing ratios. Emulsions were prepared using these surfactant systems and were assessed  
20 according to the criteria listed above (see Table I). All of the emulsions based on the vinsol resins displayed totally unacceptable stability, (that is the emulsions inverted, produced massive crystallization or gross syneresis on storage at ambient temperatures over periods of time from 1 hour to 2 weeks.

25 Due to the unacceptable performance of the vinsol resin anionic surfactants different types of anionic emulsifiers were investigated. Fatty acids neutralised with amine or metal salts in combination with fatty amine ethoxylates were found to yield emulsions with improved stability. Different fatty acids, including oleic acid, linoleic acid, lauric acid, stearic were assessed in combination with fatty amine ethoxylates of various HLB values. Emulsions were prepared using combinations of fatty acids and amine ethoxylates and the surfactants  
30 were optimised to yield the best emulsion stability.

Concomitantly fatty quaternary ammonium surfactants in combination with fatty alcohol ethoxylates were also found to yield emulsions with improved stability. However, the



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viscosity of these emulsions was too high and led to poor dispersability in water.

5 Another class of surfactants investigated was calcium dodecyl benzene sulphonate in combination with alkyl and alkylaryl polyoxyalkylene oxide ether condensates. These surfactants were found to yield emulsions with particle sizes typically less than 2µm that displayed excellent disperability and suspendability when diluted in water and good shelf stability. Again, the ratio of anionic to nonionic emulsifier was adjusted to optimise emulsion stability. (see Table I).

10 The resulting emulsion using bitumen as the controlled release matrix had a viscosity of 1500 cp. The droplet size of the emulsion was typically less than 2 µm. After two months storage at ambient temperature there was no sign of trifluralin crystallization, droplet coalesce or emulsion deterioration as determined by techniques well known in the art.

15 For bitumen matrix at high oil ratios we departed from the conventional art by dissolving all nonionic and ionic emulsifier components in the aqueous phase. This preferred method was found to yield emulsions of superior stability with smaller particle size, less prone to crystallization. It is thought that dissolving the surfactants in the aqueous phase enables rapid migration of surfactants to the interface and hence minimization of particle size.

20 The conventional art as applied to bitumen containing emulsions discloses the use of certain anionic surfactants (eg vinsol mixed with oleic and neutralised to pH 12) or blends of anionic and nonionic surfactants (eg ameroxyl OE10 (high HLB), plus vinsol neutralised to pH 12 in the aqueous phase, and Ameroxyl OE2 (low HLB) in the non-aqueous phase. The purpose of neutralising vinsol to PH12 was to promote the anionic character of the emulsifier. The role of the nonionic surfactant was to achieve a degree of steric stabilisation. This was not achieved to an adequate extent because the conventional systems were shown to be unstable (Table 1).

**TABLE 1**  
**CHARACTERISTICS OF BITUMEN EMULSIONS**

Surfactant System									
Nonionic Type	%	Ionic Type	%	% Phasing after 2 weeks	Presence of Crystallization	Common Particle Size Range (um)	Colour	Dispersability In Water	
Fatty C <sub>17</sub> alcohol/6 ethylene oxide	80	Vinsol Resin	20	20	-	Large drops >100	Dark Brown	Very Poor	
Fatty C <sub>17</sub> alcohol/6 ethylene oxide	89	Vinsol Resin	20	6	2 weeks crystals throughout	1-40	Dark Brown	Poor	
Medium chain alkyl phenol propoxylate/ethoxylate	40	Calcium Dodecyl Benzene Sulphonate	60	0	-	<1	Pale Brown	Excellent	
Medium chain alkyl phenol propoxylate/ethoxylate	50	Calcium Dodecyl Benzene Sulphonate	50	0	-	<1	Pale Brown	Excellent	
C <sub>18</sub> fatty amine/5 ethylene oxide	50	Tall Oil Fatty Acid + NaOH	50	0	-	2-20	Dark Brown	Good	

The stability of surfactant systems was investigated by looking at classes of surfactants which were anticipated to promote a sufficient degree of steric stabilisation and charge stabilisation in the dispersed phase and promote fine droplet size. Surfactants were selected on the basis of the following characteristics:

- 5        Ionic surfactants displaying low water solubility, molecular weight in the range of from 100-400 a.m.u. It was thought that surfactants displaying the above characteristics would provide a uniform charge distribution over the dispersed particle droplets and promote good interfacial packing with elected non-ionic emulsifiers.

- 10       Non-ionic surfactants with relatively high molecular weight (1500-4000), high HLB (12-17), and potential multiple anchoring sites to promote strong adhesion to the dispersed particle surface. For example alkyl phenol propoxylates/ethoxylates are suitable.

- 15       Blends of anionic and non-ionic surfactants displaying the above characteristics were mixed to optimum ratios. Optimum ratios were determined by screening the different blends of anionic and non-ionic surfactants using criteria (i-iv) as described above. Ratios of between 80:20 to 20:80 anionic:nonionic were found to work. For example using bitumen/trifluralin preferably surfactant ratios of from 60:40 to 40:60 were utilised (see Examples 4 and 5). The most preferred anionic:nonionic surfactant ratio was 50:50 (Example 6).

- 20       It is believed that the above ratios worked because the propylene oxide block in the nonionic surfactant provides multiple anchoring sites on the dispersed particles which promote strong adhesion characteristics to the particles and allowed the ethylene oxide component of the nonionic surfactant to effectively stabilise the droplets through steric stabilisation and helped reduce interfacial tension between the aqueous phase and non-aqueous phases. This is also thought to help to promote fine particle size.

- 25       It is thought that the choice of anionic surfactant provides for an even distribution of low level charge sufficient to assist stabilisation of the emulsion particles but not high enough to affect viscosity of the emulsion. It is for the above reasons that the combination of the two anionic and nonionic surfactants described above are thought to pack together at the interface and by so doing stabilise the emulsion droplets. Preferred anionic surfactants are calcium dodecyl benzene sulphonate, metal and amine salts of fatty acids (especially linoleic and oleic), resin acids and high molecular weight polyacrylic acid stabilisers.
- 30

Above-mentioned blends of anionic and nonionic surfactants, albeit at varying ratios were found to be efficient for synthesis of the following emulsions:

- I.                trifluralin in abietic acid together with volatile and non volatile solvents.

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2. chlorpyrifos in abietic acid and in resin based on the condensation of glycerol and abietic acid, together with volatile and non-volatile solvents.
3. metolachlor in bitumen, together with volatile and non-volatile solvents.

Typically the particle size of the disperse phase is less than 50 microns diameter and more usually less than 10 microns and even more usually less than 5 microns diameter. The formulations may also comprise one or more solvents for the active ingredient. Such solvents may be volatile, eg xylene and Solvesso 100, Solvesso 150 or Solvesso 200 and 1,1,1 trichloroethane, or non-volatile such as paraffin or oleic acid or water-immiscible liquids with ester functionality. Solvesso 100, 150 and 200 are proprietary high aromatic volatile hydrocarbon solvents having different boiling point ranges. Solvesso is a trademark of Shell Australia. Examples of non-volatile liquids are esters of phthalic acid and of other fatty acids e.g. oleic acid and of abietic acid, and oligomeric and polymeric condensates of di-acids such as condensates of adipic acid and polyethylene glycol. The preferred esters are lower alkyl esters of oleic and abietic acid and the most preferred are methyl oleate and ethyl oleate. The above-mentioned blends of surfactants (at various ratios) were also found useful for non-bitumen emulsions.

The relative proportions of the viscous oil, active ingredient, surfactants, and solvents if present, are important to the working of the invention. The insoluble phase, being the combination of viscous oil and active is 10-80% w/w of the composition, more preferably 30-75% and most preferably 50-70%. It should be noted however that these percentages relate to compositions in the form that they are manufactured and transported. Clearly the lower the concentration of water present in the composition the more cost efficient are transport and packaging costs. In the most preferred compositions the water level is less than 30% by weight. However, compositions of the present invention may be diluted by the applicator of the formulation by typically 30 parts of water to 1 part of controlled release formulation.

The active ingredient is selected from the range of agricultural chemicals consisting of herbicides, fungicides, nematocides and insecticides. Preferably the active ingredient has a melting point less than 140°C, more preferably less than 100°C and most preferably <80°C.

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Especially preferred herbicides are the dinitroaniline class, particularly trifluralin, and the chloroacetanilide class, particularly metolachlor. Preferred insecticides are the organophosphate class, particularly chlorpyrifos. In the compositions of the present invention the preferred levels of active are 3-70% w/w and most preferably 10-55%.

- 5      The volatile solvent e.g. Solvesso 150 is used up to 50% w/w more preferably up to 35% w/w and most preferably up to 25% w/w of the composition.

- The non-volatile solvent is preferably a water insoluble liquid having ester functionality, e.g. phthalate di-esters or polyesters comprising adipic acid residues. More preferably the non-volatile solvent is selected from the group consisting lower alkyl esters of fatty acids or abietic acid, particularly methyl and ethyl esters.
- 10

Preferably the non-volatile solvent is used up to 40% w/w, more preferably up to 20% and most preferably up to 12%.

- The aqueous phase of the formulation may contain additives to control the rheology and cold temperature storage properties of the dispersion. Examples of such additives are polyhydric alcohols such as glycerol, ethylene glycol, propylene glycol, sorbitol, polyethylene glycol and polypropylene glycol. Aqueous dispersions of the present invention are generally prepared by preparing a homogenous blend of the active ingredient and the viscous oil together with the water insoluble solvents if present. Usually heating these components to approximately 80-90°C facilitates the preparation of the blend. The surfactants, water soluble solvents and modifiers are dissolved in water by heating, preferably to 70-90°C to provide an aqueous phase. The aqueous phase is then added to under high shear conditions to the oil phase, or vice versa.
- 15
- 20

The invention will be further described by reference examples of preferred embodiments in which the compositions are expressed as part by weight.

25      BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings are graphs illustrating the results of experiments described in the following examples, which illustrate the invention.

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- Fig I relates to Example I,  
Figs 2a and 2b relate to Example 2,  
Figs 3a and 3b relate to Example 3,  
Figs 4a and 4b relate to Example 4,  
5 Figs 5a and 5b relate to Example 7,  
Fig 6 relates to Example 8,  
Fig 7 relates to Example 9,  
Figs 8a and 8b relate to Example 10,  
Figs 9a and 9b relate to Example 11,  
10 Fig 10 relates to Example 13,  
Fig 11 relates to Example 14,  
Figs 12a and 12b relate to Example 15.

#### EXAMPLE 1

#### FORMULATION A

- 15 BENEFIT OF FORMULATION: REDUCED PHYTOTOXICITY TO WHEAT

#### MATERIALS

The viscous oil used as the matrix was bitumen of type C170 (free of propane-deasphalted tar). This bitumen is defined in the Australian Standard AS2341, entitled "Properties of Residual Bitumens for Pavements".

- 20 Trifluralin (technical material) was supplied by Nufarm Pty Ltd, Pipe Road, Laverton, Victoria, Australia.

- One of the surfactants used to form and stabilise the bituminous dispersion was calcium dodecyl benzene sulphonate (CaDDBS, 68% in butanol) as supplied by Nufarm Pty Ltd under the trademark Dobenz CA. This surfactant has a HLB of  $11 \pm 1$ . The non-ionic  
25 surfactant\* is a medium chain length alkyl polyoxypropylene polyoxyethylene surfactant, having a HLB of 16.

METHOD OF FORMULATION OF DISPERSION

The dispersion consisted of:

5	a. Oil Phase	Trifluralin	144
		Bitumen C170	264
		Xylene	72
		Dobenz CA	16
		Non-ionic surfactant*	16
	b. Aqueous Phase	Water	1,120

10 The oil phase components were heated together in a 1 litre container with mixing and the temperature was allowed to rise to 100°C. The container was periodically weighed and xylene lost by evaporation was replaced. When the oil phase was homogenous, it was poured into the water phase (water temperature 85°C), which was contained in a 2 litre container. Throughout the addition of oil phase to water phase, the system was agitated using a Silverson L4R high shear mixer, with an emulsor screen attached. After 5 minutes. 15 the emulsion was cooled to 40°C using an ice bath.

BIOASSAY PROTOCOL (PHYTOTOXICITY)

The bioassay protocol for the determination of phytotoxicity of the formulation was as follows.

20 Punnets (140 x 85 x 50 mm<sup>3</sup>) were filled with 500g of soil, previously prepared to a standard moisture content depending on the soil type. This moisture was 11% for an acidic sandy loam, as typical of Wonwondah, Victoria, Australia. The soil moisture was 19% for a medium grey clay as typical of Doon, Victoria, Australia, and was 11% for an alkaline sandy loam, as typical of the Mallee, Victoria, Australia. The punnets were sprayed with trifluralin formulations at a range of rates spanning 0-1,500g trifluralin/ha through a 25 laboratory boom sprayer. The boom passes over the punnets at 6 km/hr and delivers the water plus herbicidal formulation at 64 litres/ha through spraying systems (R) nozzles 11001 at 200 kPa.

30 Immediately after spraying, the soil in each punnet was mixed thoroughly in individual plastic bags and then returned to the punnets, and sown to wheat. The punnets were then transferred to a glasshouse where they were maintained at 16°C and 24°C for 8 and 16 hours respectively, for 10 days, being watered daily to avoid moisture stress.

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5 The effect of the herbicide was assessed 10 days after spraying by determining the percentage of wheat seedlings which had emerged from the treated soil. A dose versus response curve was obtained for each formulation by fitting a line through the means of each of the six replicates. Formulations were deemed to have improved crop safety if substantially more wheat seedlings had emerged at any given application rate than from the standard emulsifiable concentrate formulation of trifluralin (40% active by weight).

#### RESULTS OF EXAMPLE 1

The results are tabulated in Table 2 and graphed in Figure 1.

10 It is apparent from Figure 1 that in the Mallee soil type used, the use of Formulation A led to substantially higher emergence of wheat seedlings compared to the EC (emulsifiable concentrate, 40% actives) which is the standard formulation supplied by Nufarm Australia). This result demonstrates that Formulation A has significantly lower phytotoxicity to wheat.



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TABLE 2

PHYTOTOXICITY: EMERGENCE OF WHEAT VERSUS RATE (MALLEE SOIL) -  
EC VERSUS FORMULATION A

5	Rate (l/ha)	Log (rate +)	% Emergence	
			EC	Formulation A
	0	0	86	86
	1.0	0.3	53	75
10	2.0	0.48	10	28
	3.0	0.6	5	10

EXAMPLE 2TRIFLURALIN CONTROLLED RELEASE FORMULATION B15 BENEFIT OF FORMULATION: REDUCED PHYTOXICITY TO WHEATMATERIALS AND METHOD OF FORMULATION OF DISPERSION

The oil phase of the formulation consisted of:

	Trifluralin	144
	Bitumen C170	68
20	Xylene	72
	Di-isodecyl phthalate	96
	Nonionic surfactant*	24
	Dobenz CA	16

The water phase consisted of water 1120 parts by weight.

25 The method of preparing the dispersion was the same as for Example 1.

\*see Example I

BIOASSAY PROTOCOL (PHYTOTOXICITY): As for Example 1.

RESULTS OF EXAMPLE 2

The results are tabulated in Tables 3a and 3b and graphed in Figures 2a and 2b.

It is apparent from Figures 2a and 2b that on both soil types studied the use of formulation B led to a substantially higher emergence of wheat seedlings compared to the EC at most application rates. This result demonstrates that Formulation B is significantly less phytotoxic to wheat.

TABLE 3a

PHYTOTOXICITY: EMERGENCE OF WHEAT VERSUS RATE (DOOEN SOIL) -  
EC VERSUS FORMULATION B

10

Rate (l/ha)	Log (rate +1)	% Emergence	
		EC	Formulation B
0	0	97	97
1.0	0.3	33	44
2.0	0.48	8	12
3.0	0.6	5	11

15

TABLE 3b

20

PHYTOTOXICITY: EMERGENCE OF WHEAT VERSUS RATE (MALLEE SOIL) -  
EC VERSUS FORMULATION B

Rate (l/ha)	Log (rate +1)	% Emergence	
		EC	Formulation B
0	0	86	86
1.0	0.3	35	62
2.0	0.48	3	33
3.0	0.6	3	9

25

30

EXAMPLE 3TRIFLURALIN CONTROLLED RELEASE FORMULATION

BENEFIT OF FORMULATION: Reduced loss of trifluralin vapour to the atmosphere.

5 This example uses the same formulation as Example 2, but shows a different benefit of the formulation.

BIOASSAY PROTOCOL (VOLATILE LOSS OF ACTIVE)

The bioassay protocol for the determination of efficacy of the trifluralin formulations was as follows:

10 Soil was air dried and brought to a given level of water by weight (see bioassay protocol: phytotoxicity). The soil was placed into containers of dimension 85mm x 140mm x 50mm (depth) and the containers of soil were sprayed at rates of formulation in the range 0-1.5 litres/hectare of trifluralin emulsifiable concentrate. The standard emulsifiable concentrate formulation contained 40% trifluralin active. A spray volume of 60 litres/hectare of water was used, and the dilute formulation were sprayed through Spraying System nozzles of type  
15 11003 using 200 kilopascals of air pressure. Ambient temperature was  $30 \pm 3^{\circ}\text{C}$ .

The sprayed containers were treated in two ways:

- a. Soil was immediately mixed thoroughly after spraying to effect instant and complete incorporation of active, and returned to the container.
- b. Sprayed soil was left for 48 hours, then mixed as above.

20 The treated soil portions were bioassayed for trifluralin according to the following protocol.

Soil portions were sown at 24 hours after spraying with 20 seeds of annual ryegrass (*Lolium rigidum*) to a depth of 1 cm. The samples were kept at 18-22°C in a glasshouse for 10 days, and were watered twice daily. The results were obtained by calculating the percentage emergence from each container of soil.

25 The results are tabulated and are graphed using points which represent the mean value of six duplicates. The graphs are presented as % emergence vs  $\log_{10}(\text{dose} + 1)$ . The numerical value for the dose is in units of litres per hectare equivalent of trifluralin

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emulsifiable concentrate.

In general, efficacy results for controlled release formulations are compared with efficacy results for the emulsifiable concentrate standard formulation sprayed at the same time.

- 5 The difference between the dose response curves corresponding to treatment (a) (immediate incorporation), and (b) (incorporation at t=48 hours) was taken to be related to the extent of volatile loss of active. A decrease in this difference would indicate reduced volatile loss.

### RESULTS OF EXAMPLE 3

The results are tabulated in Tables 4a and 4b, and graphed in Figures 3a and 3b.

- 10 Figure 3a shows the results for EC, which should be compared with Figure 3b which gives the results for Formulation B. In all these experiments, the soil used was medium grey clay (Dooen).

It was concluded that the loss of efficacy caused by the delay in incorporation was significantly less when Formulation B was used.

15

TABLE 4a

#### VOLATILISATION EXPERIMENT: EMERGENCE OF WEEDS VERSUS RATE DOOEN SOIL: IMMEDIATE AND DELAYED INCORPORATION - TRIFLURALIN EC

Rate (l/ha)	Log (rate + 1)	% Emergence	
		Imm. Inc	Del. Inc
0	0	86	90
1.0	0.08	60	80
2.0	0.15	11	42
3.0	0.20	15	41
1.0	0.30	1	16
1.5	0.40	0	2

TABLE 4b

VOLATILISATION EXPERIMENT: EMERGENCE OF WEEDS VERSUS RATE  
DOOEN SOIL: IMMEDIATE AND DELAYED INCORPORATION - FORMULATION B

5	Rate (l/ha)	Log (rate - 1)	% Emergence	
			Immediate Inc.	Delayed Inc.
10	0	0	88	90
	0.2	0.08	55	90
	0.4	0.15	5	20
	0.6	0.20	1	14
	1.0	0.30	0	5
	1.5	0.40	0	1

15 EXAMPLE 4

TRIFLURALIN CONTROLLED RELEASE FORMULATION C

BENEFIT OF FORMULATION: REDUCED PHYTOTOXICITY TO WHEAT

MATERIALS (SEE EXAMPLE 1)

METHOD OF FORMULATION OF DISPERSION C

20	The dispersion consisted of:	
	<u>Component</u>	<u>Parts w/w%</u>
	<u>Oil Phase</u>	
	Trifluralin (technical grade)	20.26
	Bitumen C170 PD Tar free	35.80
25	Xylene	11.48
	<u>Aqueous Phase</u>	
	Water	24.65
	Dobenz CA	2.09
	nonionic surfactant* (see Example I)	1.39
30	Glycerol	4.33

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The oil phase was prepared by blending the melted bitumen and trifluralin and xylene until homogenous at 90°C.

The aqueous phase was prepared by dissolving the components in the water at 80°C.

5 The oil phase was heated to 100°C prior to emulsification. The aqueous phase (80°C) was added to the oil phase and emulsified using a Silverson homogenizer with a 16mm disintegrating head at 2/3 maximum speed for 2 minutes.

10 The resulting emulsion had a viscosity of 1500 cp. The droplet size of the emulsion was typically less than 2  $\mu$ m. After two months storage at ambient temperature there was no sign of trifluralin crystallization, droplet coalescence or emulsion deterioration as determined by techniques well known in the art.

Formulation C was the same as Formulation A in terms of matrix composition but the oil phase ratio percentage much higher.

BIOASSAY PROTOCOL (PHYTOTOXICITY): See Example 1

#### RESULTS OF EXAMPLE 4

15 The results are tabulated in Tables 5a and 5b and are graphed in Figures 4a and 4b.

It is apparent from Figures 4a and 4b that on both soil types studied at Doon and Mallee respectively, the use of Formulation C led to a higher emergence of wheat seedlings compared to the EC at most application rates. This demonstrates that Formulation C was significantly less phytotoxic to wheat.

20

TABLE 5a

PHYTOTOXICITY: EMERGENCE OF WHEAT VERSUS RATE

DOON SOIL: EC VERSUS - FORMULATION C

Rate (l/ha)	Log (rate + 1)	% Emergence	
		EC	F o r m u l a t i o n C
0	0	90	90
1.0	0.30	43	60
2.0	0.48	2	20
3.0	0.06	3	12

TABLE 5b

PHYTOTOXICITY: EMERGENCE OF WHEAT VERSUS RATE  
MALLEE SOIL: EC VERSUS - FORMULATION C

5	Rate (l/ha)	Log (rate + 1)	% Emergence	
			EC	F o r m u l a t i o n C
	0	0	88	88
	1.0	0.30	29	73
10	2.0	0.48	5	39
	3.0	0.06	2	10

EXAMPLE 5

15 An emulsion of the type suitable for use as a pre-emergent herbicide was prepared using the following components according to the procedure below.

	<u>Component</u>	<u>Part w/w%</u>
	<u>Oil Phase</u>	
	Trifluralin technical grade	20.26
	Bitumen PD tar free	29.29
20	Xylene	11.48
	Di-isodecyl phthalate	6.51
	<u>Aqueous Phase</u>	
	Water	28.96
	Calcium dodecyl benzene	
25	sulphonate (68% active)	2.10
	Non-ionic surfactant**	1.40

30 The non-ionic surfactant\*\* is an alkyl polyoxypropylene polyoxyethylene condensate where alkyl is C<sub>3</sub> - C<sub>8</sub>, the polyoxypropylene is 67-77 moles; and the polyoxyethylene is 70-80 moles.

The oil phase was prepared by blending the components at 90°C until fluid and homogeneous and heating to 100°C prior to emulsification.

The emulsifier was dissolved in the aqueous phase at 80°C.

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The aqueous phase was added to the oil phase and emulsified using a Silverson homogenizer with a 16 mm disintegrating head at 2/3 maximum speed for 2 minutes.

5 The resulting emulsion had a viscosity of 1800 cp. The droplet size was typically less than 2  $\mu$ m. After one month storage at ambient temperature the emulsion showed no signs of trifluralin crystallization, droplet coalescence or deterioration as determined by techniques commonly employed in the art.

#### EXAMPLE 6

An emulsion suitable for use as a pre-emergent herbicide was prepared using the following following components according to the procedure below.

10	<u>Component</u>	<u>Part w/w %</u>
	<u>Oil Phase</u>	
	Trifluralin technical grade	20.26
	Bitumen C170 PD Tar free	35.80
	Xylene	11.48
15	<u>Aqueous Phase</u>	
	Water	24.62
	Calcium dodecyl benzene	1.755
	Sulphonate (68% active)	
	Nonionic surfactant*	
20	(see Example I)	1.755
	Glycerol	4.34

The oil phase was heated to 100°C prior to emulsification. The aqueous phase (at 80°C) was added to the oil phase and emulsified using a Silverson homogenizer with a 16 mm disintegrating head for 2 minutes.

25 EXAMPLE 7

TRIFLURALIN CONTROLLED RELEASE FORMULATION D.BENEFIT OF FORMULATION:  
INCREASED POTENCY OF TRIFLURALIN



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MATERIALS

The oil phase of the formulation consisted of

	Trifluralin	96
	Chinese Rosin	72
5	(natural product substantially abietic acid ex China)	
	Solvesso 150	72
	Nonionic surfactant* (see Example I)	14
	Dobenz CA	6

10 The water phase consisted of 560 parts.

METHOD OF FORMULATION OF DISPERSION D

Trifluralin and Chinese rosin were heated together until homogeneous at 100°C and then solvesso 150 and Dobenz CA were added and stirred. This oil phase (90°C) was added to water (90°C) in the presence of high shear agitation provided by a Silverson L4R high shear mixer. Particle size was 1-3 microns.

BIOASSAY PROTOCOL: (As for volatile loss of active - see Example 3)

RESULTS OF EXAMPLE 7

The results are tabulated in Tables 6(a), 6(b) and graphed in Figs 5(a) and 5(b). Fig 5(a) shows the results for EC, which should be compared with Fig 5(b) which gives the results for Formulation D. For all these experiments the soil used was an alkaline sandy loam as typical of the Mallee, Victoria, Australia.

It was concluded that Formulation D was significantly more potent than was the EC both under conditions of immediate and delayed incorporation.

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TABLE 6(a)

TRIFLURALIN ECPOTENCY EXPERIMENT - EMERGENCE OF WEEDS ON RATE.MALLEE SOIL. IMMEDIATE AND DELAYED INCORPORATION.

5

Rate (l/ha)	Log <sub>10</sub> (rate + 1)	% Emergence	
		Imm. Inc.	Del. Inc.
0	0	90	95
0.1	0.05	90	90
0.2	0.09	94	90
0.3	0.12	72	82
0.4	0.15	41	70
0.6	0.2	19	73
0.8	0.26	10	64
1	0.3	1	35
1.5	0.4	3	22

TABLE 6(b)

20

TRIFLURALIN FORMULATION D.POTENCY EXPERIMENT - EMERGENCE OF WEEDS ON RATE. MALLEE SOIL.IMMEDIATE AND DELAYED INCORPORATION.

25

Rate (l/ha)	Log <sub>10</sub> (rate + 1)	% Emergence	
		Imm. Inc.	Del. Inc.
0	0	90	95
0.1	0.05	89	92
0.2	0.09	92	90
0.3	0.12	47	78
0.4	0.15	28	84
0.6	0.2	8	48
0.8	0.26	8	33
1	0.3	3	10
1.5	0.4	1	3

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EXAMPLE 8TRIFLURALIN CONTROLLED RELEASE FORMULATION EBENEFIT OF FORMULATION: REDUCED PHYTOTOXCITY TO WHEATMATERIALS AND METHOD OF FORMULATION OF DISPERSION E

5      The oil phase of the formulation consisted of

	Trifluralin	96
	Chinese rosin	48
	Solvesso 150	96
	Nonionic surfactant*	14
10	Dobenz CA	6

The water phase consisted of 560 parts. The method used was as for Example 7.

\*see Example I

BIOASSAY PROTOCOL (PHYTOTOXICITY)

As for Example I

15      RESULTS OF EXAMPLE 8

The results are tabulated in Table 7, which includes control data relating to EC, and are graphed in Fig 6.

TABLE 7

PHYTOTOXICITY: EMERGENCE OF WHEAT VERSUS RATE  
MALLEE SOIL - EC & TRIFLURALIN FORMULATION E

5	Rate (l/ha)	Log <sub>10</sub> (rate + 1)	% Emergence	
			EC	Formulation E
	0	-	98	98
	0.6	-	65	69
10	0.8	-	52	66
	1	-	47	55
	1.5	-	40	51
	2	-	12	12
	2.5	-	6	9
15				

It is apparent from Fig 6 that the use of Formulation E on Mallee soil led to a substantially higher emergence of wheat seedlings compared to EC at most application rates. This result demonstrates that Formulation E is less phytotoxic to wheat.

EXAMPLE 9

20 TRIFLURALIN CONTROLLED RELEASE FORMULATION F  
BENEFIT OF FORMULATION: REDUCED PHYTOTOXICITY TO WHEAT  
MATERIALS AND METHOD OF FORMULATION OF DISPERSION F

The oil phase of the formulation consisted of

	Trifluralin	168
25	Chinese Rosin	144
	Ester gum SA	
	(glycerol ester of abietic acid, manufactured by Frankston Manufacturing Co., Victoria)	48
	Solvesso 150	120
30	Nonionic surfactant* (see Example I)	28
	Dobenz CA	12

The water phase consisted of 1,120 parts. The method used was as for example 7.

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BIOASSAY PROTOCOL (PHYTOTOXICITY)

As for Example I.

RESULTS OF EXAMPLE 9

5 The results are tabulated in Table 8 which includes control data relating to EC, and are graphed in Fig 7.

TABLE 8

PHYTOTOXICITY: EMERGENCE OF WHEAT VERSUS RATE  
MALLEE SOIL - EC & TRIFLURALIN FORMULATION F

10	Rate (l/ha)	Log <sub>10</sub> (rate + 1)	% Emergence	
			EC	Formulation F
	0	-	98	98
	0.6	-	62	84
15	0.8	-	42	72
	1	-	39	46
	1.5	-	18	21
	2	-	3	16
	2.5	-	2	8
20				

It is apparent from Fig 7 that the use of Formulation F on Mallee soil led to a higher emergence of wheat seedlings compared to EC at most application rates. This result demonstrates that Formulation F is less phytotoxic to wheat.

EXAMPLE 10

25 TRIFLURALIN CONTROLLED RELEASE FORMULATION G  
BENEFIT OF FORMULATION: INCREASED POTENCY OF TRIFLURALIN

Materials

	Trifluralin	120
	Chinese rosin	72
30	Solvess 150	48
	Nonionic surfactant*	14
	Dobenz CA	6

The water phase consisted of 560 parts. The method was as for Example 7.

\* see Example I

BIOASSAY PROTOCOL (AS FOR VOLATILE LOSS OF ACTIVE - SEE EXAMPLE 3)RESULTS OF EXAMPLE 10

The results are tabulated in Tables 9(a), 9(b) and graphed in Figs 8(a) and 8(b). Fig 8(a) shows the results for EC which should be compared with Fig 8(b) which gives the results for Formulation G. Mallee soil was used in all experiments. It was concluded that Formulation G was significantly more potent than was the EC both under conditions of immediate and delayed incorporation.

TABLE 9 (a)TRIFLURALIN EC (40% ACTIVE)

POTENCY EXPERIMENT - EMERGENCE OF WEEDS VS RATE  
MALLEE SOIL. IMMEDIATE AND DELAYED INCORPORATION

	Rate l/ha	Log <sub>10</sub> (rate + 1)	% Emergence	
			Imm. Inc.	Del. Inc.
15	0	0	90	95
	0.1	0.05	90	90
	0.2	0.09	92	90
	0.3	0.12	94	82
20	0.4	0.15	41	70
	0.6	0.2	19	73
	0.8	0.26	10	64
	1	0.3	1	35
25	1.5	0.4	3	22

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TABLE 9 (b)

TRIFLURALIN FORMULATION GPOTENCY EXPERIMENT - EMERGENCE OF WEEDS VS RATEMALLEE SOIL. IMMEDIATE AND DELAYED INCORPORATION

5	Rate l/ha	Log <sub>10</sub> (rate + 1)	% Emergence	
			Imm. Inc.	Del. Inc.
10	0	0	90	95
	0.1	0.05	91	96
	0.2	0.09	86	91
	0.3	0.12	30	93
	0.4	0.15	19	69
	0.6	0.2	10	46
15	0.8	0.26	2	15
	1	0.3	1	7
	1.5	0.4	0	3

EXAMPLE 1120 TRIFLURALIN CONTROLLED RELEASE FORMULATION HBENEFIT OF FORMULATION: INCREASED POTENCY OF TRIFLURALINMATERIALS

25	Trifluralin	192
	Chinese rosin	48
	Solvess 150	240
	Nonionic surfactant*	28
	Dobenz CA	12

The water phase consisted of 1,120 parts. The method was as for Example 7.

\* see Example I

BIOSAY PROTOCOL (AS FOR VOLATILE LOSS OF ACTIVE - SEE EXAMPLE 3)RESULTS OF EXAMPLE 11

The results are tabulated in Tables 10(a), 10(b) and graphed in Figs 9(a) and 9(b). Fig 11(a) shows the results for EC which should be compared with Fig 9(b) which gives the results for Formulation H. It was concluded that formulation H was significantly more potent than was the EC.

TABLE 10 (a)TRIFLURALIN EC (40% ACTIVE)POTENCY EXPERIMENT: EMERGENCE OF WEEDS VS RATE10 MALLEE SOIL - IMMEDIATE AND DELAYED INCORPORATION

	Rate l/ha	Log <sub>10</sub> (rate + 1)	% Emergence	
			Imm. Inc.	Del. Inc.
15	0	0	95	85
	0.1	0.05	97	87
	0.2	0.09	73	77
	0.3	0.12	34	89
	0.4	0.15	20	84
20	0.6	0.2	5	60
	0.8	0.26	2	32
	1	0.3	1	18
	1.5	0.4	0	3



TABLE 10 (b)TRIFLURALIN FORMULATION HPOTENCY EXPERIMENT: EMERGENCE OF WEEDS VS RATEMALLEE SOIL - IMMEDIATE AND DELAYED INCORPORATION

5

	Rate l/ha	Log <sub>10</sub> (rate + 1)	% Emergence	
			Imm. Inc.	Del. Inc.
	0	0	95	80
10	0.1	0.05	85	85
	0.2	0.09	55	92
	0.3	0.12	10	86
	0.4	0.15	6	81
	0.6	0.2	2	40
15	0.8	0.26	1	10
	1	0.3	0	2
	1.5	0.4	0	3

EXAMPLE 12

- 20 An emulsion suitable for use as a pre-emergent herbicide was prepared using the following components according to the procedure below.

	<u>Component</u>	<u>Part</u>
	<u>Oil Phase</u>	
	Trifluralin	26
25	Chinese rosin	19.5
	Solvesso 150	19.5
	Dobenz CA	0.5
	<u>Water phase</u>	
	Water	28.5
30	Polyethyleneglycol (MW300)	4
	Nonionic surfactant*	2

\* see Example I

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METHOD

In a 1 litre container were added 240 g of trifluralin and 180 g of Chinese rosin, and heated to 105°C with stirring until homogeneous. Weight loss was 1.5 g (0.36%). 180 g of Solvesso 150 was added and the mixture was stirred, the temperature thereby dropping to 75°C. The mixture was further stirred until the temperature reached 58°C. Weight loss was 0.5 g which was replenished by Solvesso 150. The mixture was decanted into jars which were tightly sealed. The mixture remained liquid at -5°C.

- In a 100 ml beaker was added 0.4 g of Dobenz CA and 52 g of the above-mentioned mixture (oil phase), and heated with stirring to 95°C.
- 10 The water phase was prepared by adding 1.6 g nonionic surfactant\* 3.2 g of PEG 300 and 22.8 g of boiling water to a 100 ml beaker.

- The beaker containing the water phase was agitated using the 16 mm disintegrating head on a Silverson homogenizer. The oil phase was gradually added, and care was taken to ensure that the surface of the liquid in the beaker was continuously homogenised by adjusting the height of the disintegrating head. When addition of the oil phase was complete, the emulsion was further homogenised for 30 minutes.
- 15

\* see Example I

EXAMPLE 13METOLACHLOR FORMULATION I

The emulsion in this example contained the herbicide metolachlor which is of the chloro acetanilide class.

5     MATERIALS

	Metolachlor	36
	Bitumen C170, PD tar free	42
	Di-isodecyl phthalate	24
	Xylene	18
10	Nonionic surfactant*	6
	Dobenz CA	4

The water phase consisted of 280 parts.

\* see Example I

METHOD

- 15     Metolachlor, bitumen, di-isodecyl phthalate and nonionic surfactant were mixed at 110°C until homogeneous. Xylene and Dobenz CA were added and the weight loss replenished using xylene. The above oil phase was slowly added to water which was agitated using a Silverson homogenizer.

BIOASSAY PROTOCOL

- 20     This protocol was as for the volatile loss of active in Example 3 with the following modifications:
- 25     (i)     The metolachlor was sprayed through a laboratory sprayer capable of simulating field conditions. Applications were at a pressure of 200 kpa, through nozzles giving a 100 degree flat fan in 64 l/ha water and at 6 kilometres per hour.
- (ii)    Formulations were applied at 0, 18, 36, 72, 144, 216, 288 and 432 g metolachlor/ha.
- (iii)   All treatments were incorporated immediately after spraying and punnets were then each sown to 25 seeds of annual rye grass (*holium rigidum*).
- (iv)   Treatments were assessed for emergence 10 days safter spraying and all seedlings with a height in excess of 20 mm were counted as having satisfactorily emerged.

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RESULTS OF EXAMPLE 13

The results are tabulated in Table 11 and graphed in Fig 10. Fig 10 also shows control data for the performance of EC (Dual, 72% active supplied by Ciba-Geigy Australia) which should be compared with Formulation I. It was concluded that Formulation I was significantly more potent than EC.

TABLE IIMETOLACHLOR FORMULATION I

POTENCY EXPERIMENT - EMERGENCE OF WEEDS VS RATE.  
MALLEE SOIL. IMMEDIATE INCORPORATION. EC (72% ACTIVE)  
AND METOLACHLOR FORMULATION I

	Rate (l/h)	Log <sub>10</sub> (rate +1)	EC	% Emergence Metol. I
	EC equivalent			
15	0	-	90	90
	0.03	-	95	85
	0.06	-	95	93
	0.11	-	93	84
	0.2	-	70	41
20	0.3	-	37	14
	0.4	-	20	4

Example 14METOLACHLOR FORMULATION J

BENEFIT OF FORMULATION: Increased potency of metolachlor.

MATERIALS

	Metolachlor	36
	Bitumen CI70 PD tar free	66
	Xylene	18
30	Nonionic surfactant*	6
	Dobenz CA	4

The water phase consisted of 280 parts.

\* see Example I

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METHODS

As for Example 13.

BIOASSAY PROTOCOL

As for Example 13.

5 RESULTS OF EXAMPLE 14

The results are tabulated in Table 12 and graphed in Fig 11. Fig 11 also shows control data for the performance of EC which should be compared with Formulation J. It was concluded that Formulation J was significantly more potent than EC.

TABLE 1210 METOLACHLOR FORMULATION J

POTENCY EXPERIMENT - EMERGENCE OF WEEDS VS RATE.  
MALLEE SOIL. IMMEDIATE INCORPORATION. EC (72% ACTIVE)  
AND METOLACHLOR FORMULATION J

15	Rate (l/h)	Log <sub>10</sub> (rate +1)	% Emergence	
	EC equivalent		EC	Metol. J
20	0	-	90	90
	0.03	-	95	90
	0.06	-	95	81
	0.11	-	93	88
	0.2	-	70	31
	0.3	-	37	10
	0.4	-	20	3
25				

EXAMPLE 15CHLORPYRIFOS FORMULATION K

BENEFIT OF FORMULATION: Reduced volatile loss of chlorpyrifos.

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MATERIALS

	Chlorpyrifos (technical, ex Nufarm)	6
	Rosin ester	2l
	Nonionic surfactant*	l.l
5	Dobenz CA	l.9

The water phase consisted of 70 parts of water and 0.1 parts keltrol, a cellulosic thickener consisting of a high molecular weight xantham gum made by Kelco Division of Merc & Co USA.

\* see Example I

10 METHOD

Nonionic surfactant, rosin ester and chlorpyrifos were heated at 145°C and stirred until homogeneous. Subsequently Dobenz CA was added and the mixture was again stirred. The emulsion was formed by adding oil phase (115°C) to boiling water in the presence of high shear agitation supplied by a Silverson homogenizer. After addition of the oil phase  
15 was complete, the emulsion was cooled to 40°C and Keltrol was added with rapid agitation for a further 2-3 minutes.

BIOASSAY PROTOCOL: Reduced volatile loss(a) GLASS SUBSTRATE

Glass petri dishes were treated with 1 ml of insecticide formulation (log series from  
20  $10^{-9}$  to  $10^{-4}$  grams active ingredient/ml). Five replicates of each dose for each formulation were treated and left to dry overnight. On day 2, freshly emerged adult. Apanteles Subandinus (10 individuals) were added to each replicate plus 5 untreated controls. Mortality was assessed after 24 hours (day 3).

(b) LEAF BIOASSAY, GLASS-HOUSE

Potato plants (*S. Tuberosum*) were grown in pots in a glass-house (temperatures up  
25 to 35°C) and each plant was sprayed by hand until runoff with formulations of chlorpyrifos ( $10^{-7}$  grams active ingredient per ml). Leaves were picked on several days after spraying and bioassayed at 23°C with Apanteles Subandinus. Disks (2cm  
diameter) were cut from the leaves and placed in a glass petri dish (10 discs/petri  
30 dish) with A. Subandinus (10/dish). 5 petri dishes were used for each formulation and the control. The mortality of *A. Subandinus* was assessed as for the above bioassay.

RESULTS OF EXAMPLE 15

The results are tabulated in Tables I3(a) and I3(b) for the glass substrate and leaf bioassay respectively, and control data is also shown for the performance of the EC (Lorsban, by Dow Elanco). The results are also graphed in Figs I2(a) and I2(b). On the glass substrate test (Fig I2(a)) chlorpyrifos formulation K killed A. Subandinus at much lower dose than Lorsban. The estimated LD50 for Formulation K was two orders of magnitude lower than for Lorsban.

On the leaf substrate (glass-house) test (fig I2(b)), Lorsban killed high numbers of A. Subandinus for only one day while chlorpyrifos formulation K killed high numbers for over 7 days.

TABLE I3(a)CHLORPYRIFOS FORMULATION KVOLATILE LOSS EXPERIMENT: Glass Substrate EC (Lorsban 50) and Formulation K

Dosage (Micrograms chlorpyrifos per dish)	Percent Mortality	
	EC	Formulation K
1,000	100	100
20	100	100
2	26	100
0.2	8	90
0.02	5	8

TABLE I3(b)CHLORPYRIFOS FORMULATION KVOLATILE LOSS EXPERIMENT: Leaf Bioassay EC (Lorsban 50) and Formulation K

Days After Application	Percent Mortality	
	EC	Formulation K
1	100	100
3	25	100
9	22	75
22	0	0

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EXAMPLE I6CHLORPYRIFOS FORMULATION LBENEFIT OF FORMULATION: Reduced volatile loss of chlorpyrifosMATERIALS

5	Chlorpyrifos	48
	Rosin ester	60
	Nonionic surfactant*	6
	Dobenz CA	6
	Water	280
10	Keltrol	0.6

The method was as for Example I5.

\* see Example I

BIOASSAY PROTOCOL: Reduced volatile loss, glass substrate (as for E15)RESULTS

- 15 The results were that the estimated LD 50 for Formulation L was 2 orders of magnitude lower than for Lorsban and data are shown in Table I4.

TABLE I4CHLORPYRIFOS FORMULATION LVOLATILE LOSS EXPERIMENT - GLASS SUBSTRATE

20

	Dosage (micrograms chlorpyrifos per disk)	Percent Mortality	
		EC	Formulation L
	1,000	100	100
25	20	100	100
	2	22	100
	0.2	10	66



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Since modifications within the spirit and scope of the invention may be readily effected by persons skilled in the art, it is to be understood that the invention is not limited to the particular embodiments described, by way of example, hereinabove.

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CLAIMS

1. A controlled release composition comprising an aqueous dispersion of a water insoluble matrix as the disperse phase wherein the matrix contains at least one active ingredient selected from the group consisting of herbicides, insecticides, fungicides and nematocides, characterised in that the matrix comprises a viscous oil selected from the group consisting of bitumen, abietic acid and ester derivatives of abietic acid, carboxylic acid containing materials and carboxylic acid ester containing materials.
2. A composition according to Claim 1 wherein the active ingredient has a melting point less than 120°C.
3. A composition according to Claim 1 wherein the active ingredient has a melting point less than 80°C.
4. A composition according to any one of the preceding claims wherein the active material is either a chloroacetanilide or dinitroaniline herbicide or an organophosphate insecticide.
5. A composition according to any one of the preceding claims wherein the composition further comprises anionic and non-ionic surfactants having a HLB in the range of 8-20.
6. A composition according to Claim 5 wherein the anionic surfactant is a calcium salt of an alkyl benzene sulphonic acid and the non-ionic surfactant includes a polyethylene oxide and polypropylene oxide copolymer or copolymer adduct.
7. A composition according to any one of Claims 1 to 6 wherein the composition further comprises a non-volatile diluent having ester functionality.
8. A composition according to any one of Claims 1 to 7 wherein the composition further comprises a volatile solvent for the oil phase and wherein the ratio of said volatile solvent to active ingredient is in the range 0.5 to 1.5.
9. A composition according to any one of Claims 1 to 8 wherein the active ingredient comprises 15% by weight of the composition and the disperse phase comprises at least 50% by weight of the composition.
10. A composition according to any one of Claims 1 to 9 wherein the active ingredient is selected from the group consisting of trifluralin, chlorpyrifos and metolachlor.

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11. A method of treating soil to retard the growth of vegetation thereon, comprising applying to the soil a controlled release composition according to any one of Claims 1 to 5, wherein the active ingredient is a herbicide.
12. A method of rendering insects ineffective by using a controlled release composition according to any one of Claims 1 to 5, wherein the active ingredient is an insecticide.

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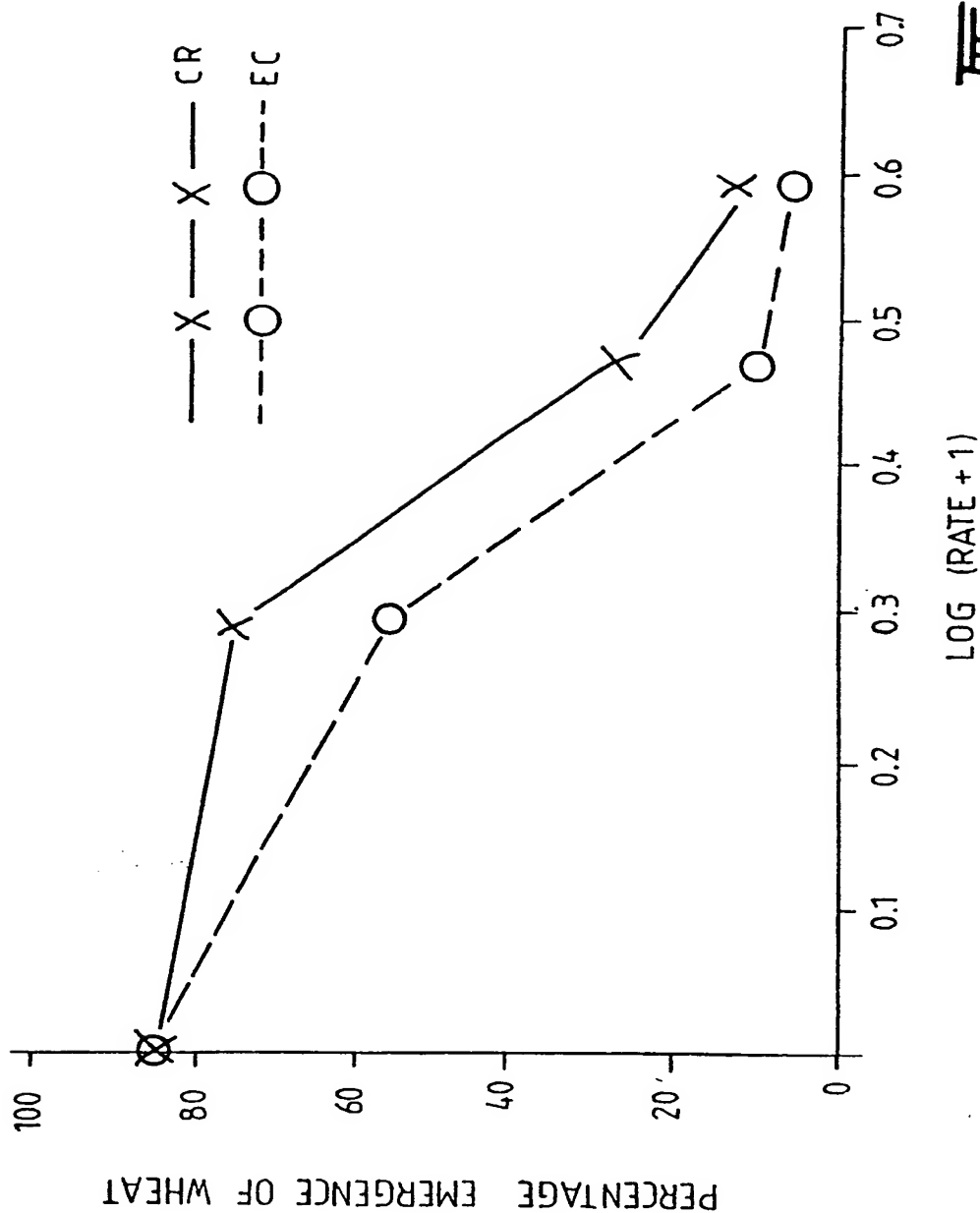


Fig. 1

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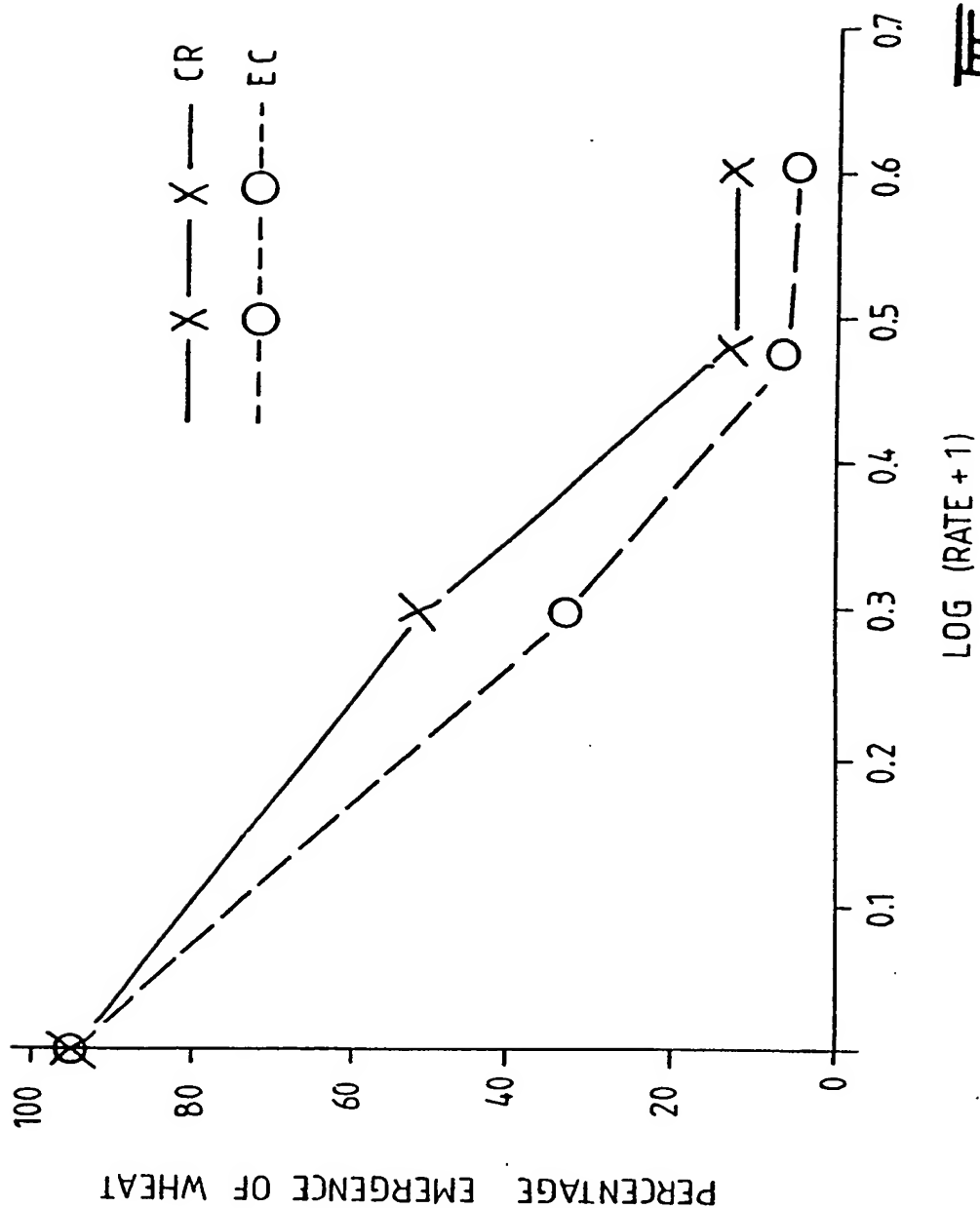


Fig. 2a.

- 3 / 19 -

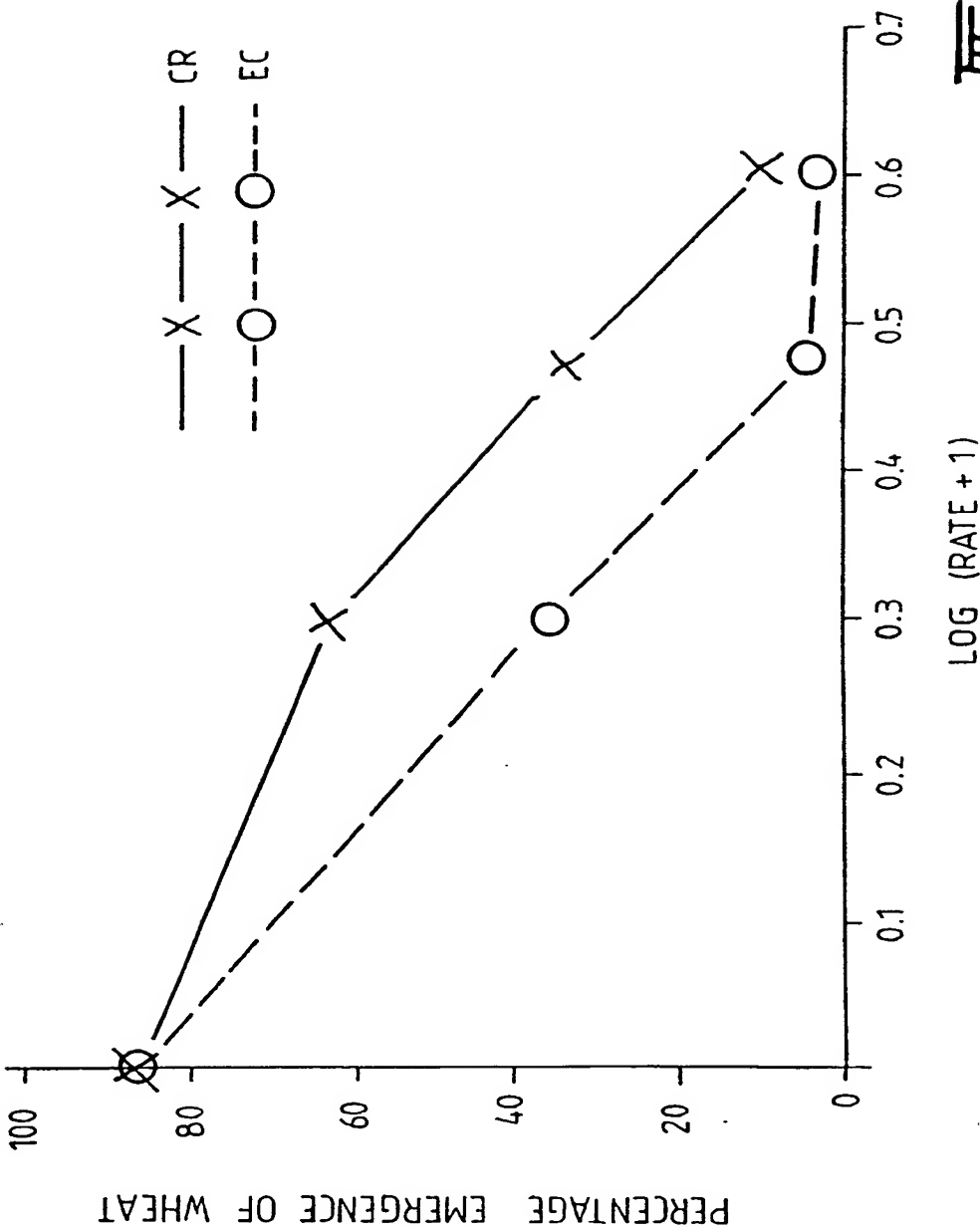
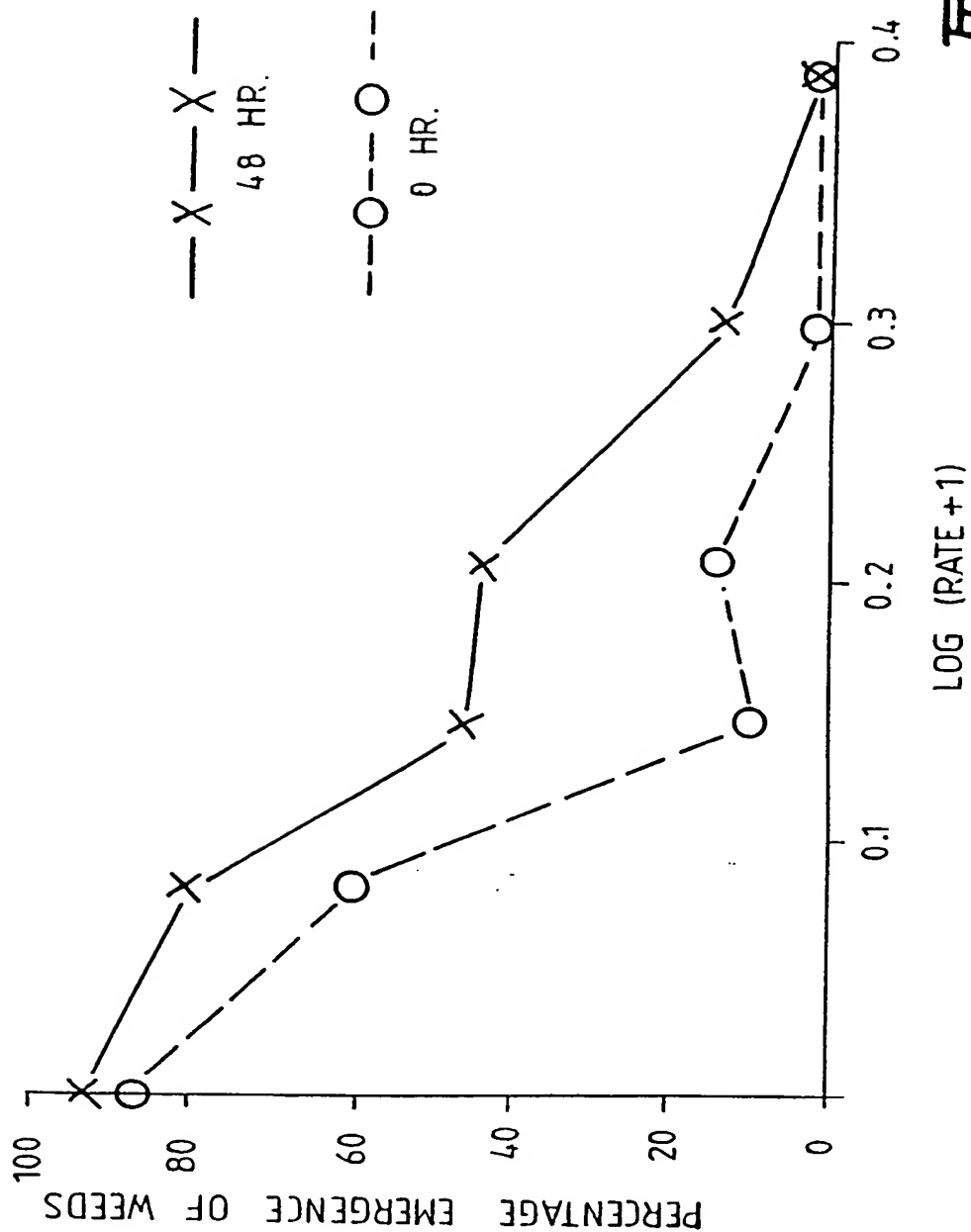


Fig. 2b.



III.3a.

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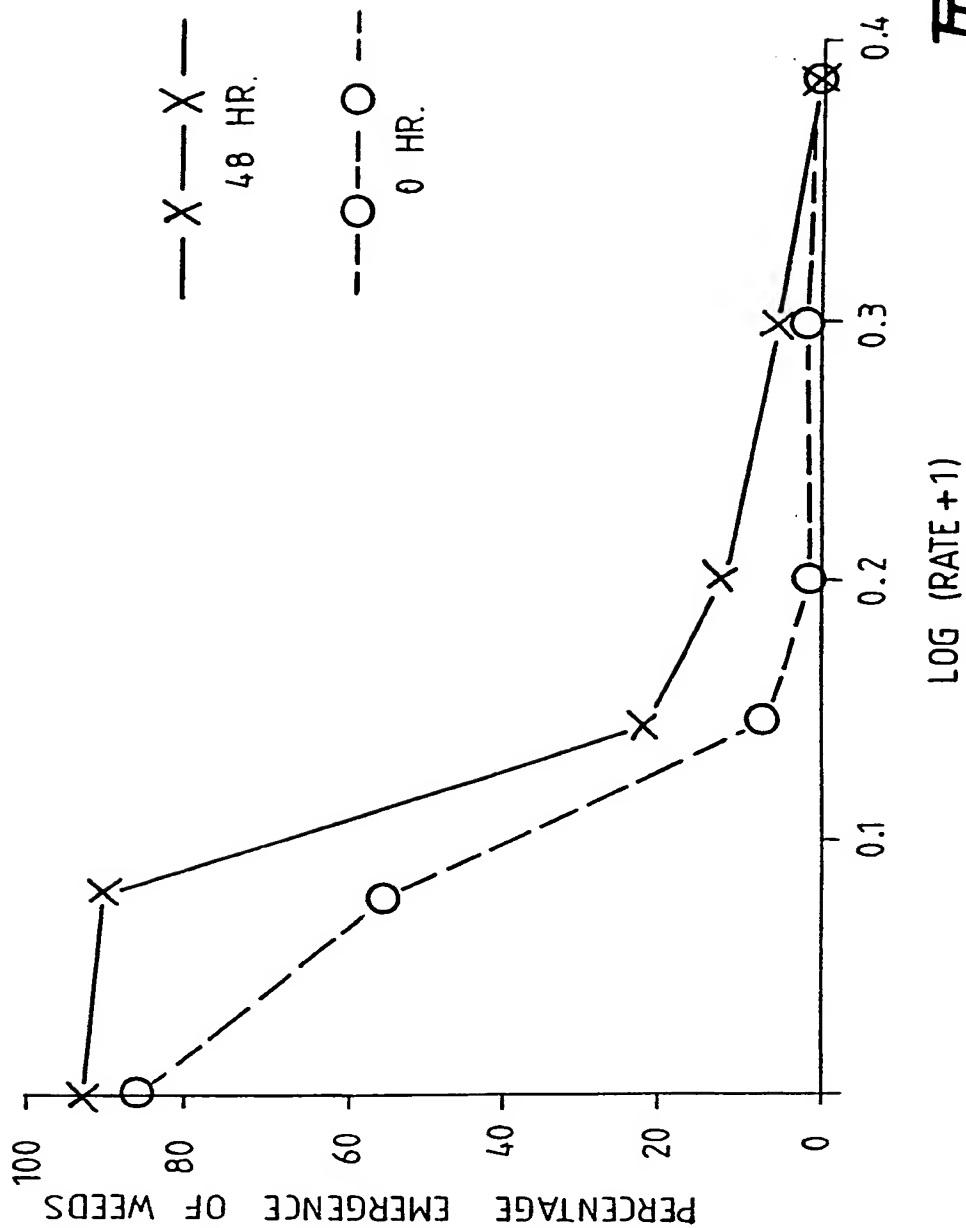


Fig. 3b.



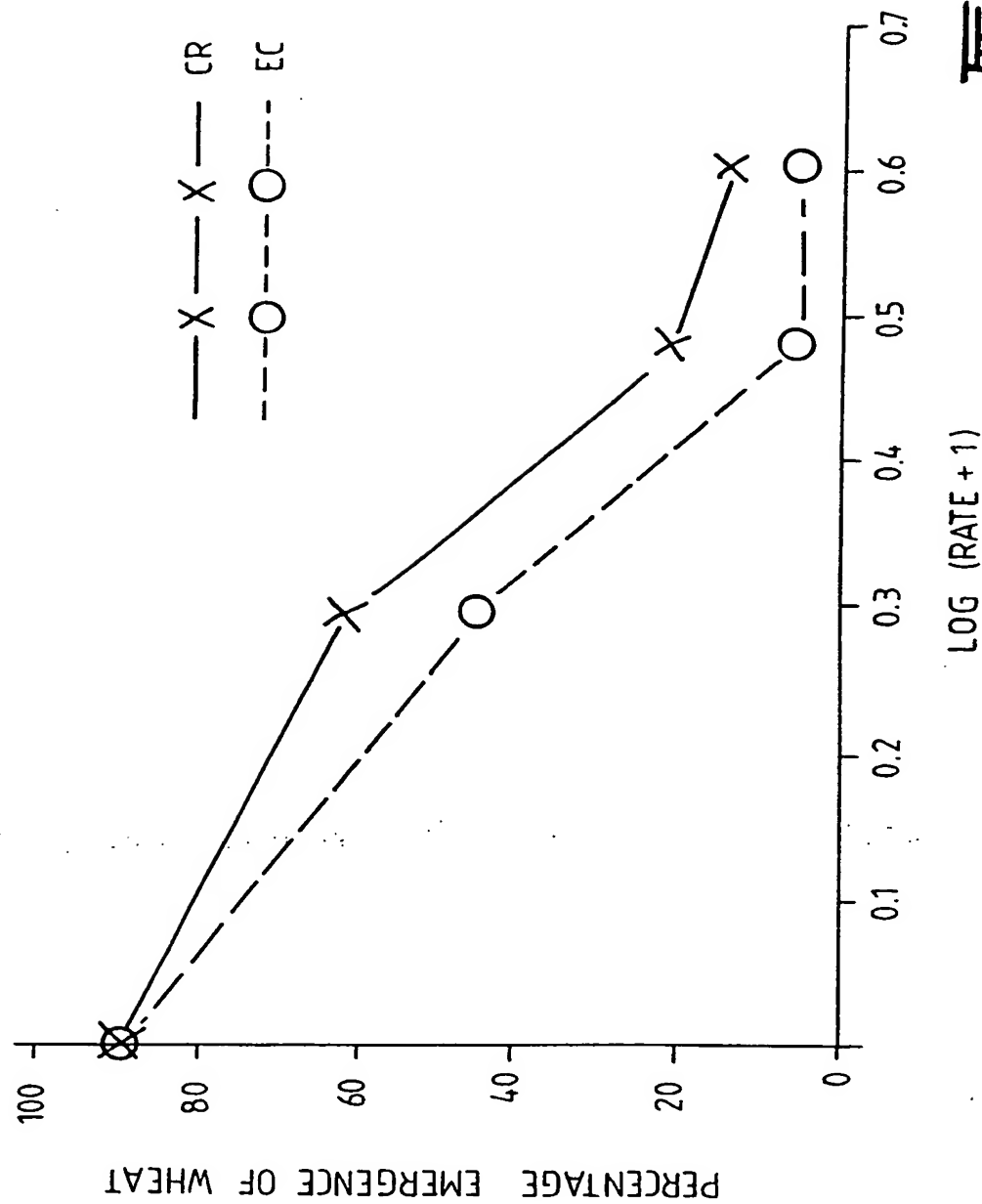
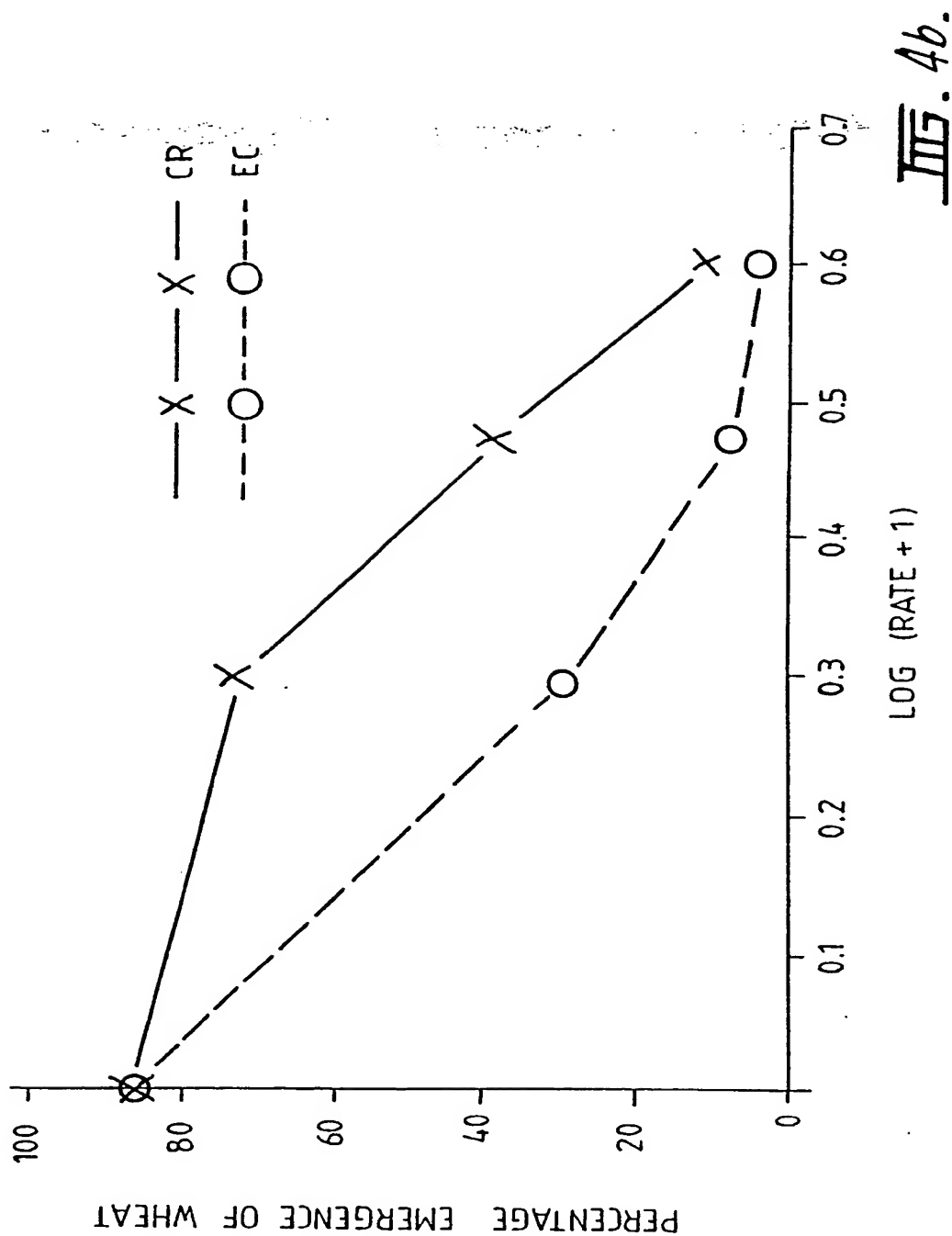
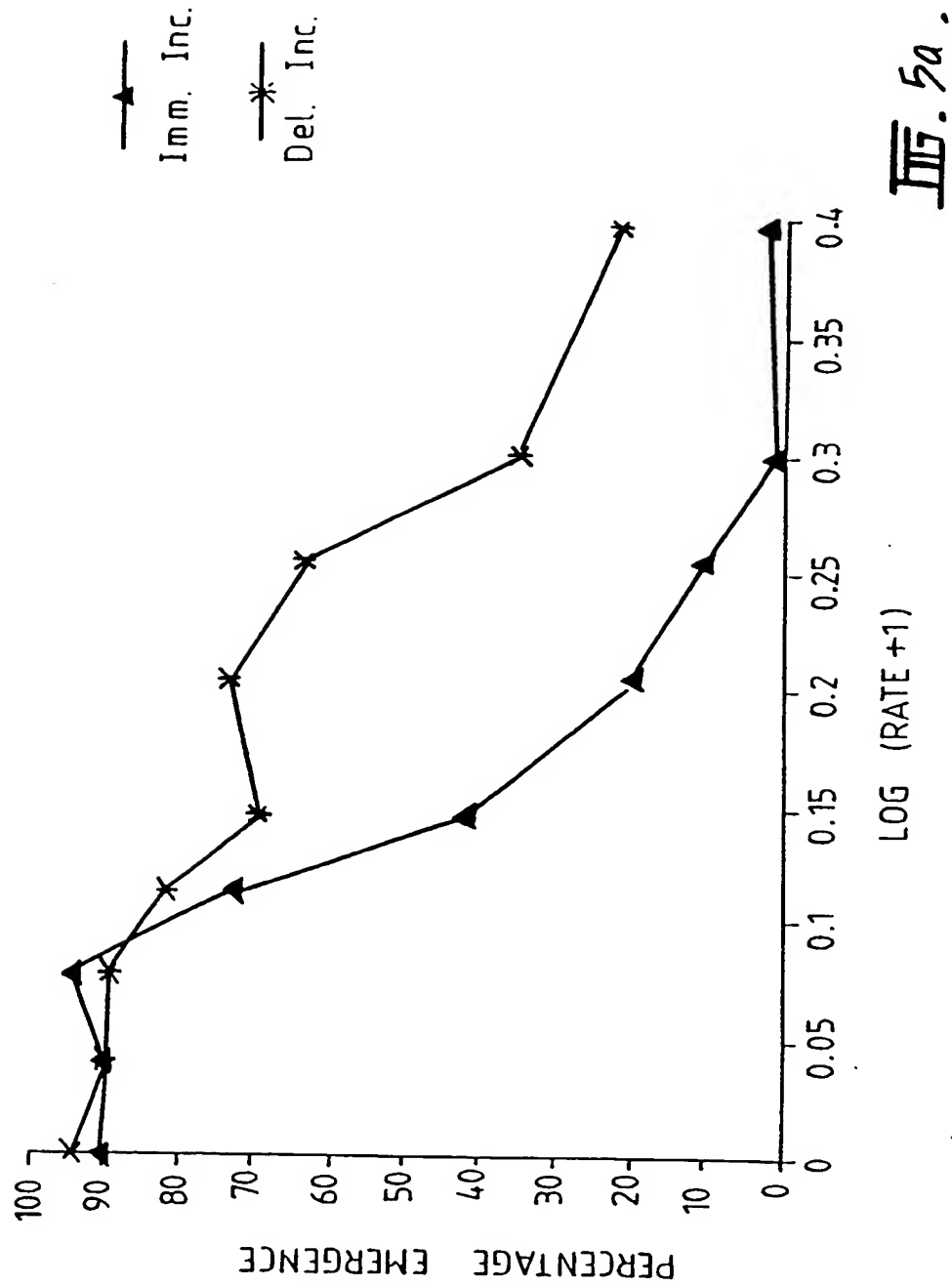


Fig. 4a.

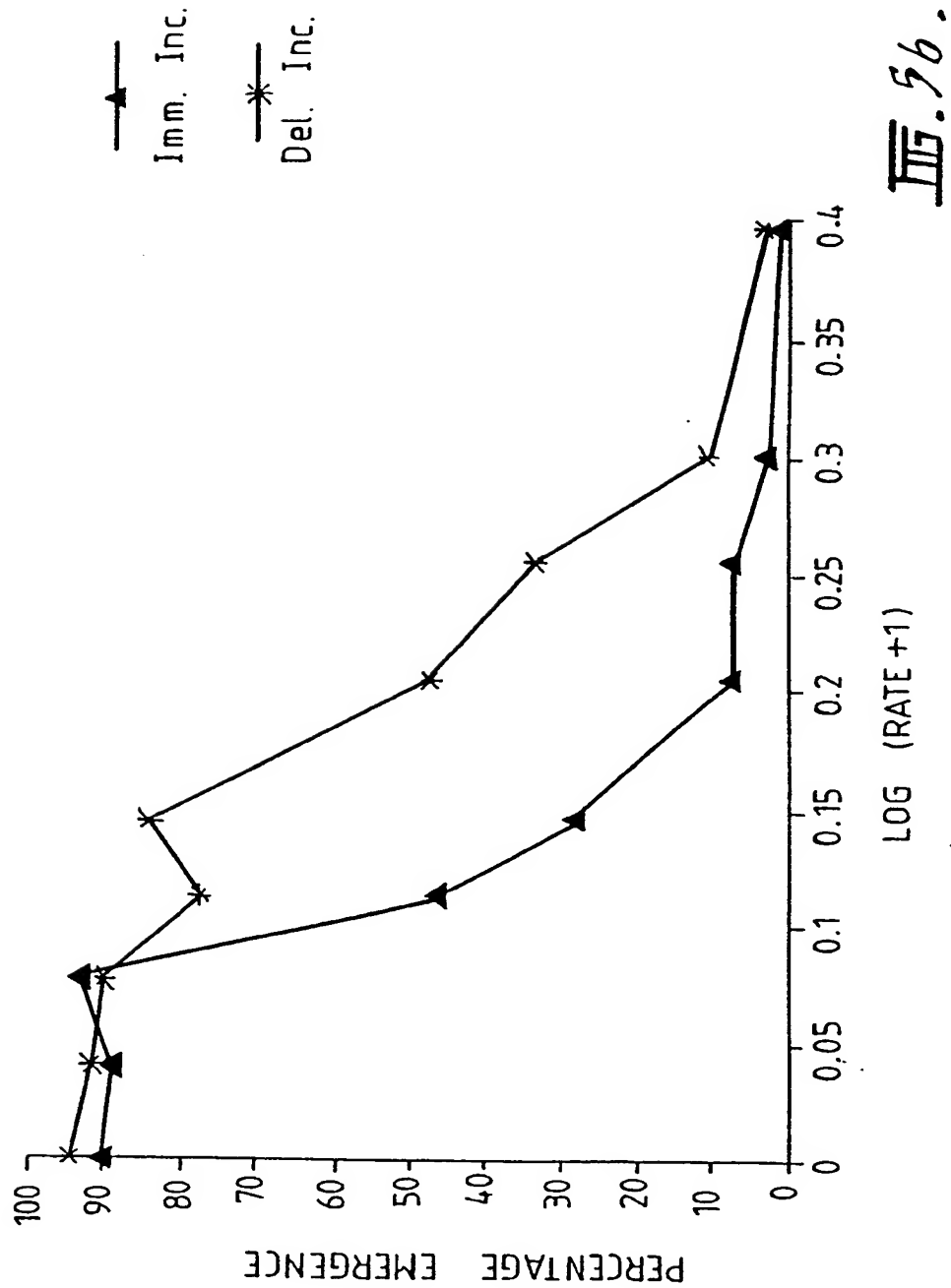
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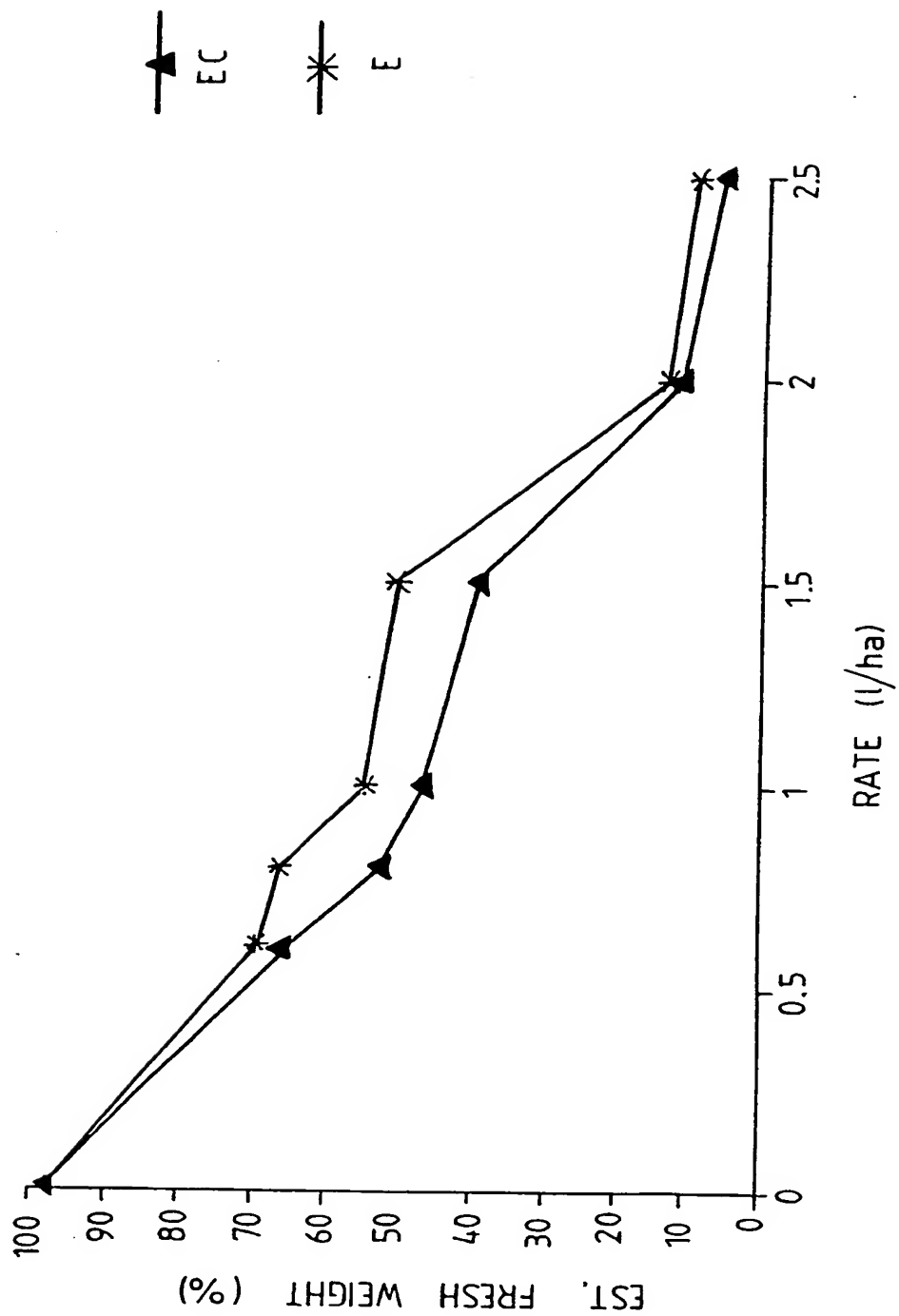


Fig. 6.

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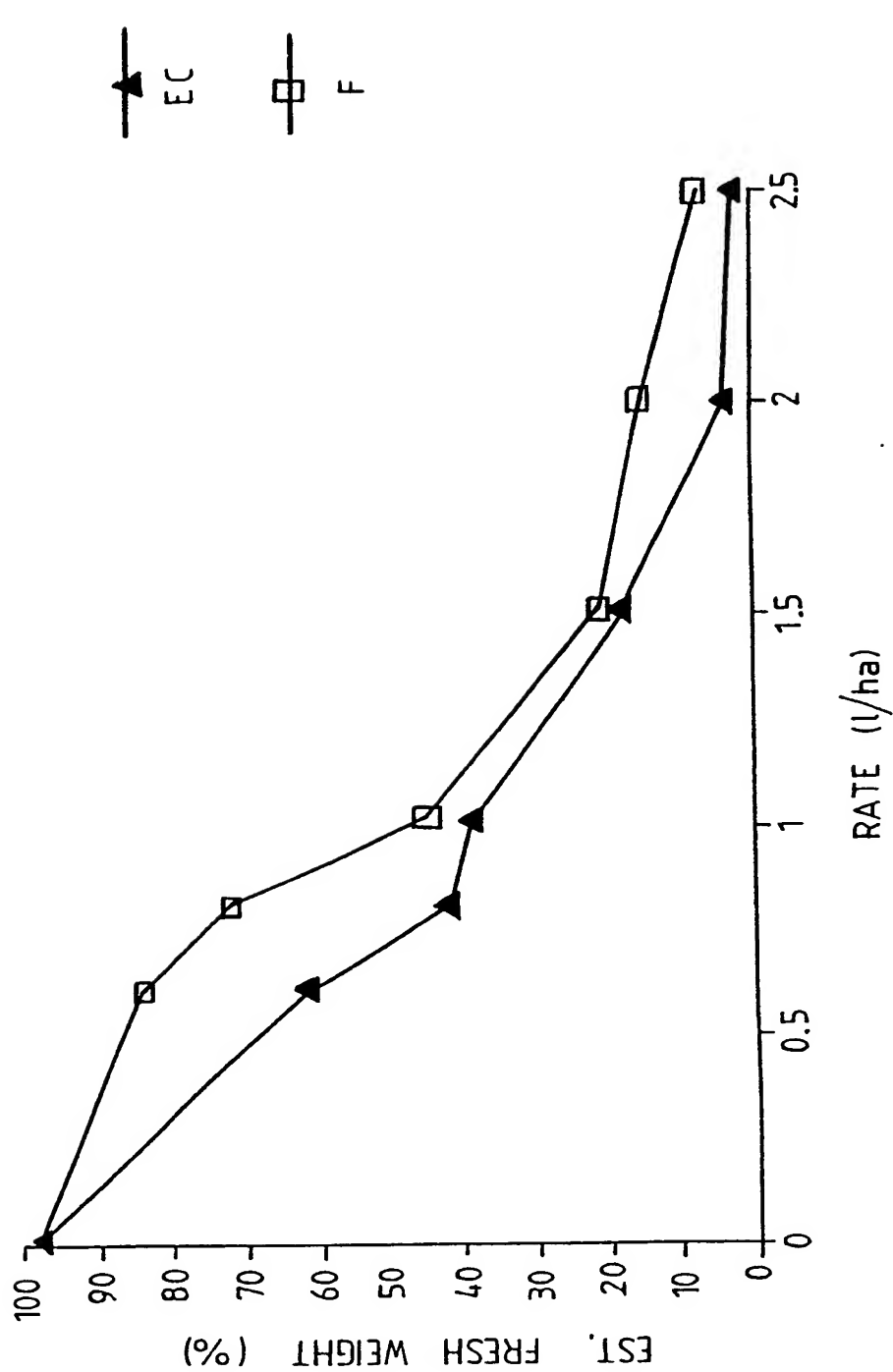
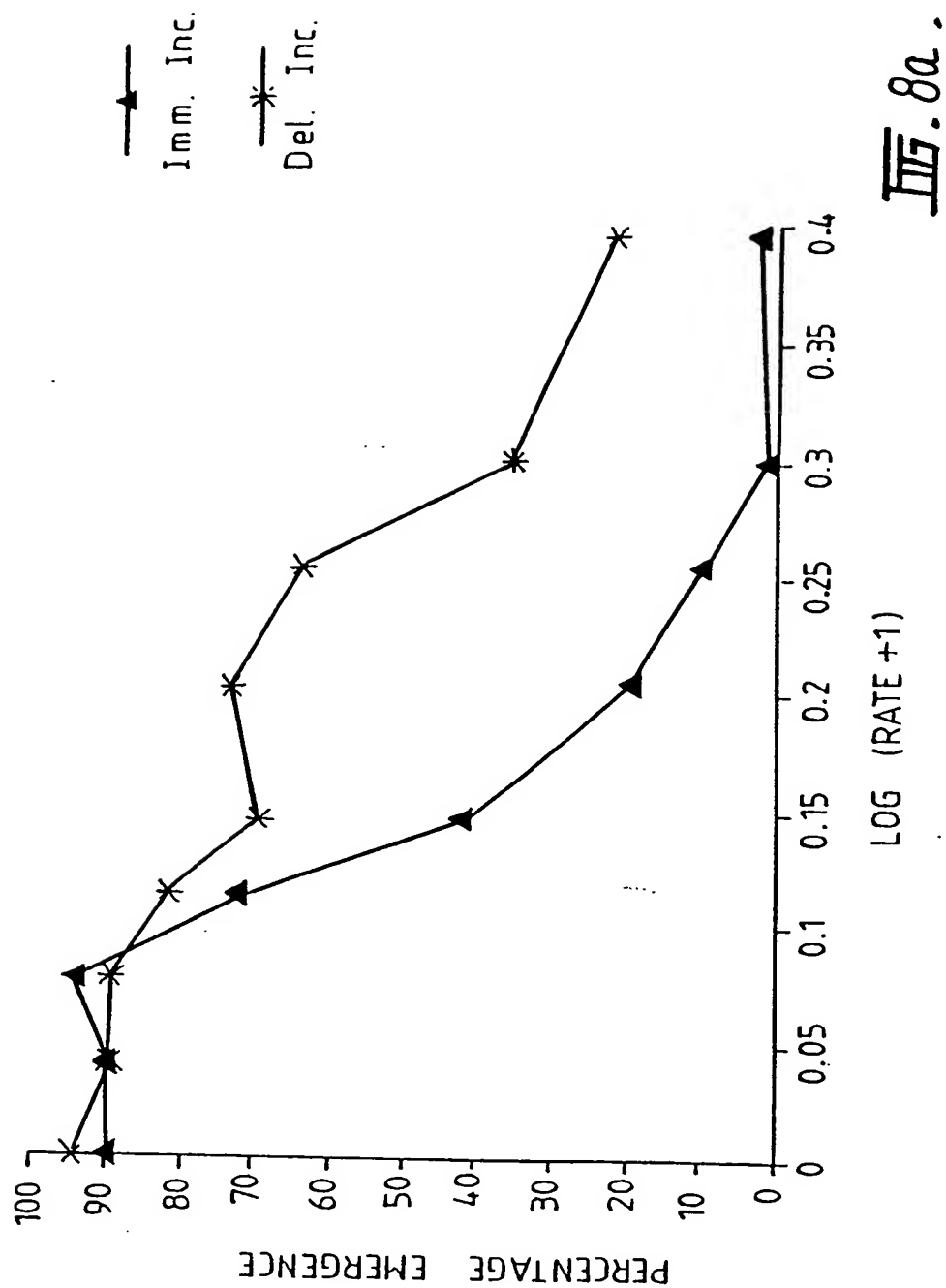


Fig. 7.

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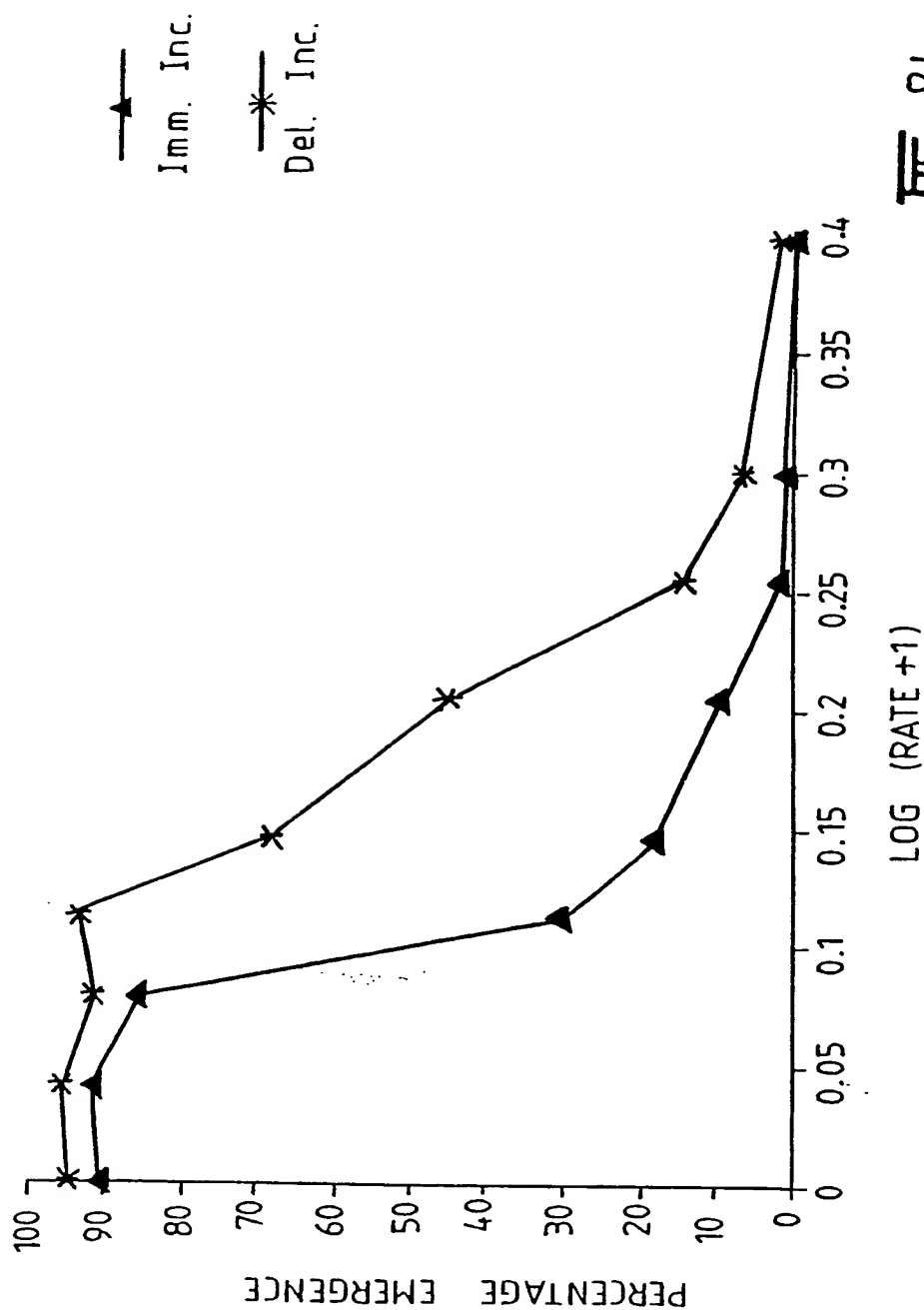


Fig. 8b.



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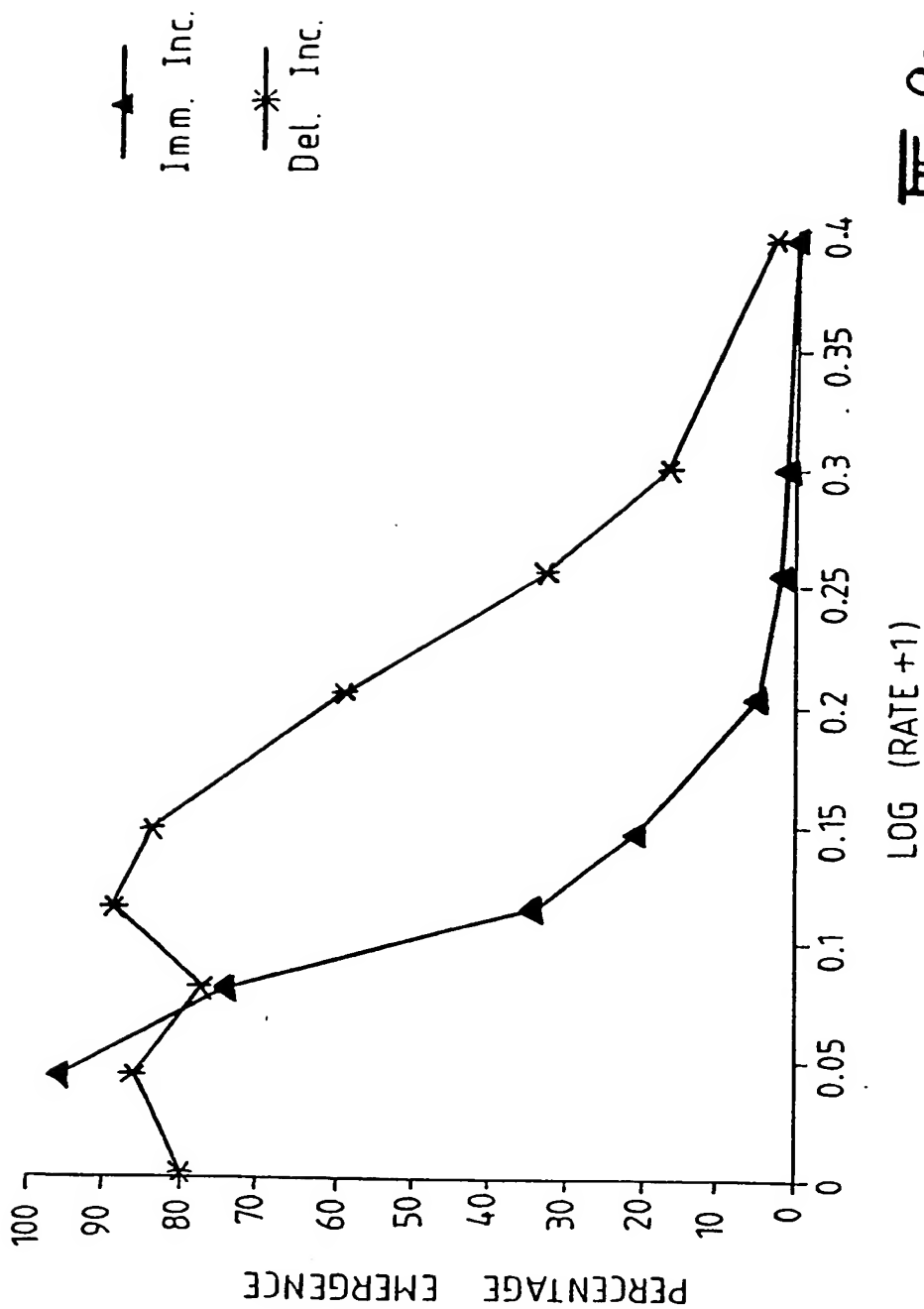


Fig. 9a.

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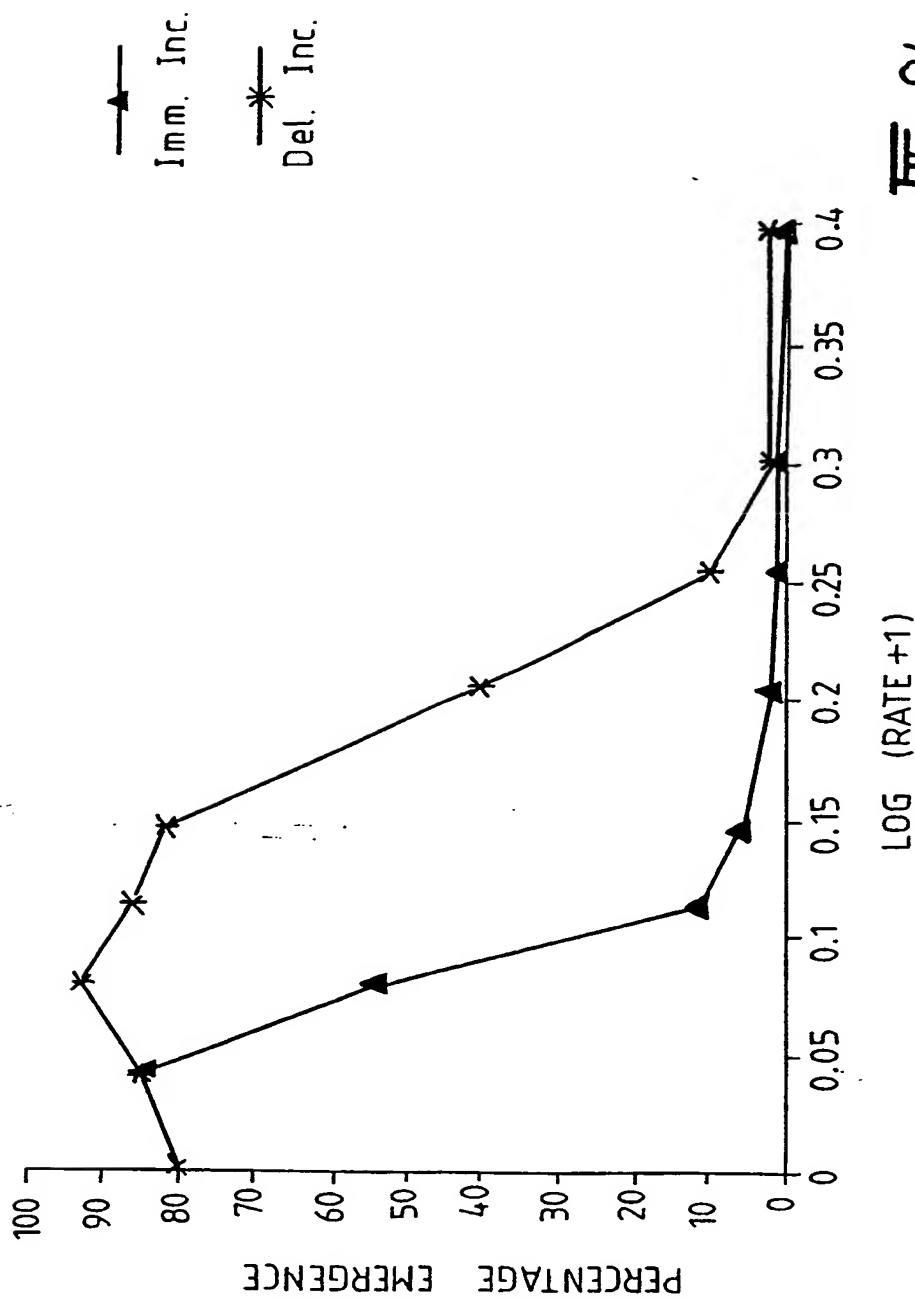


Fig. 9b.

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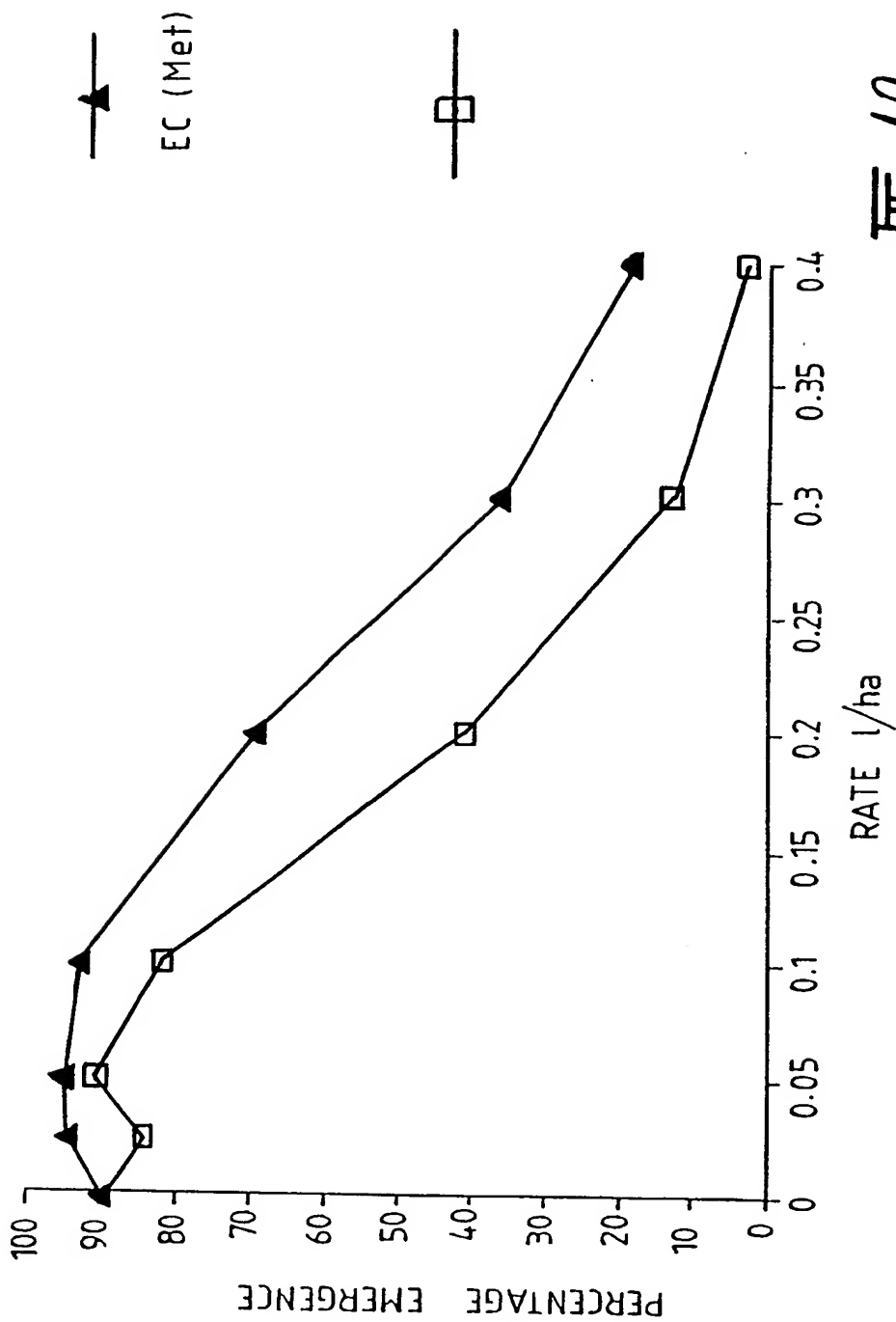


FIG. 10.

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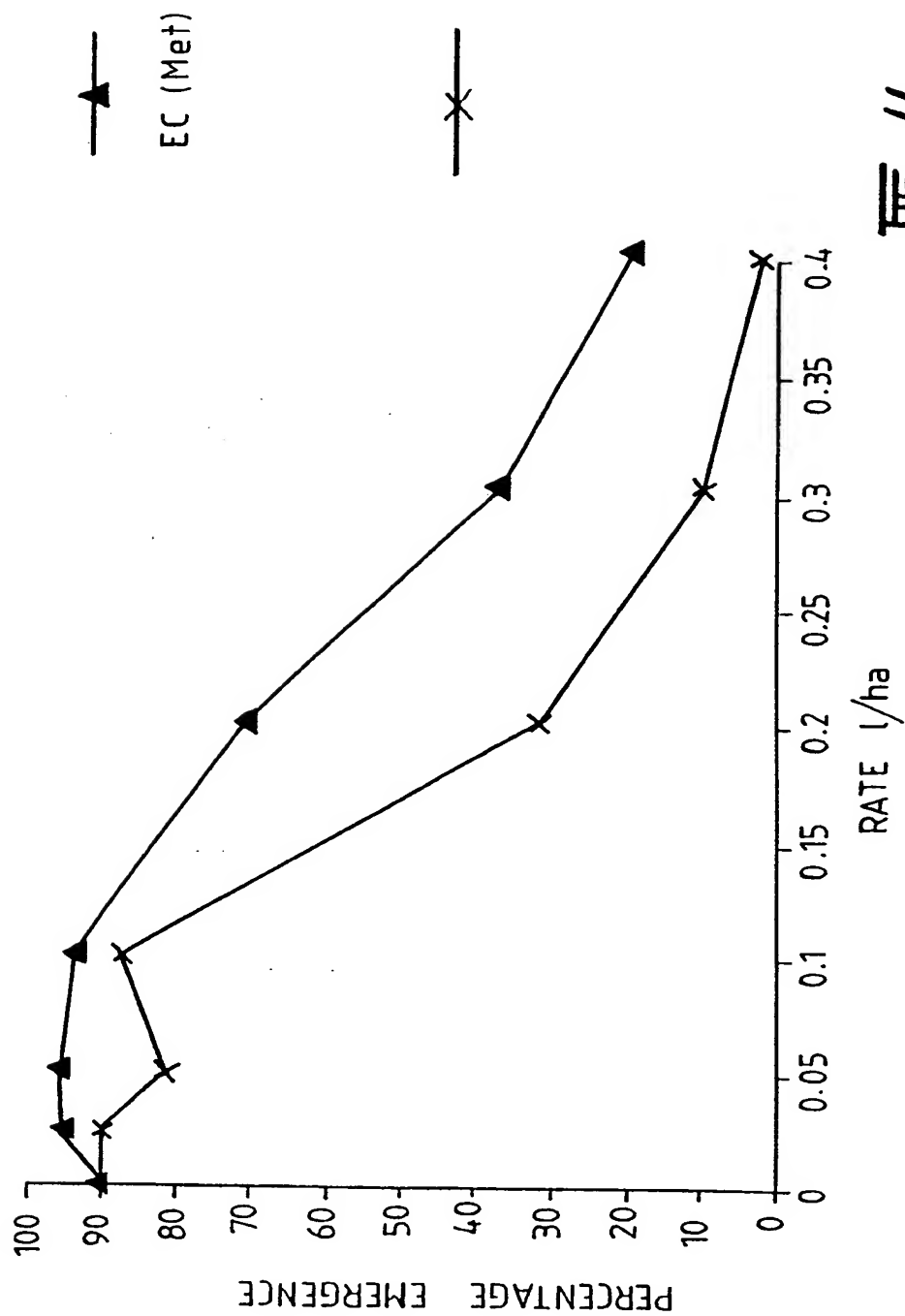
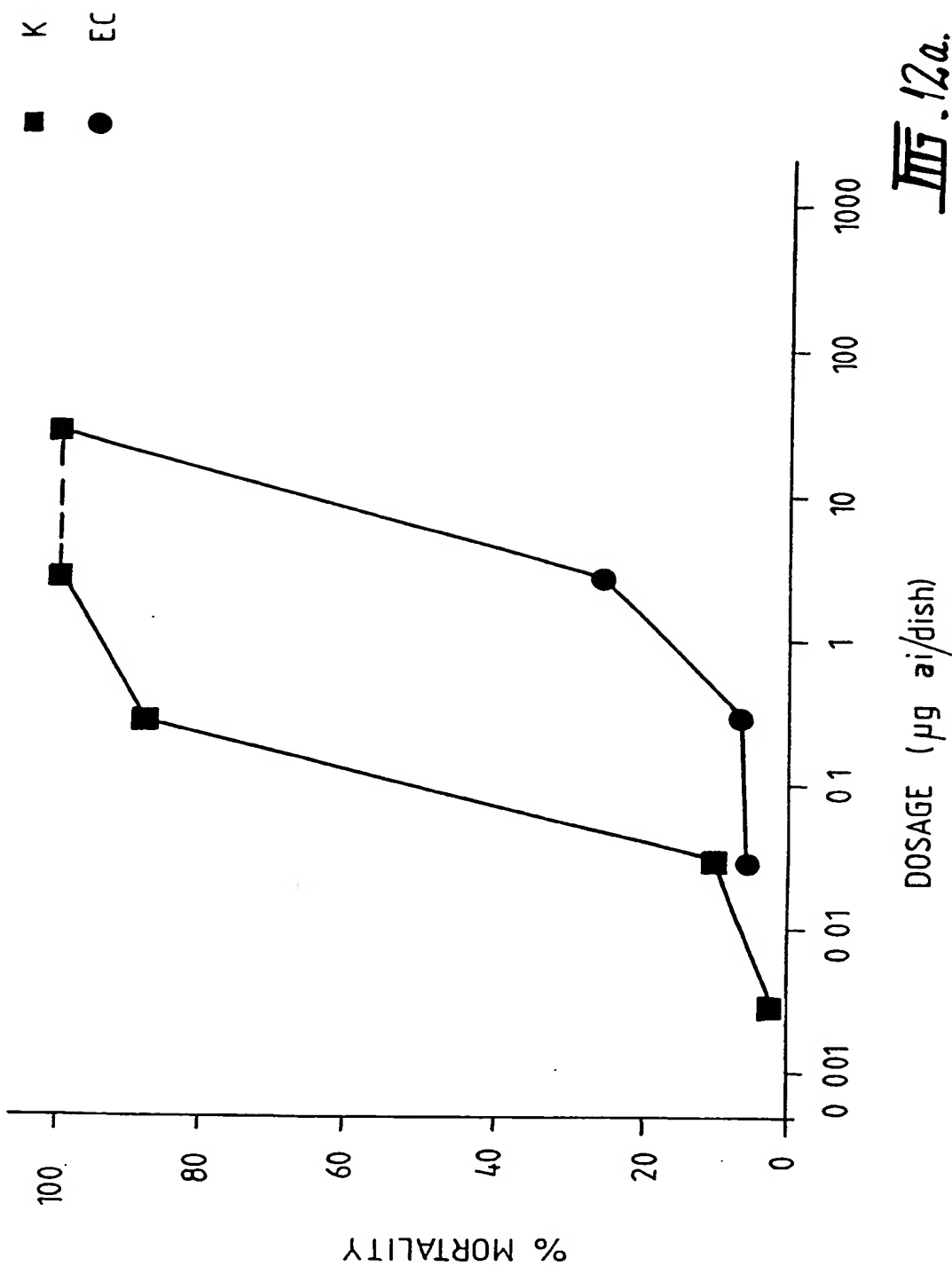
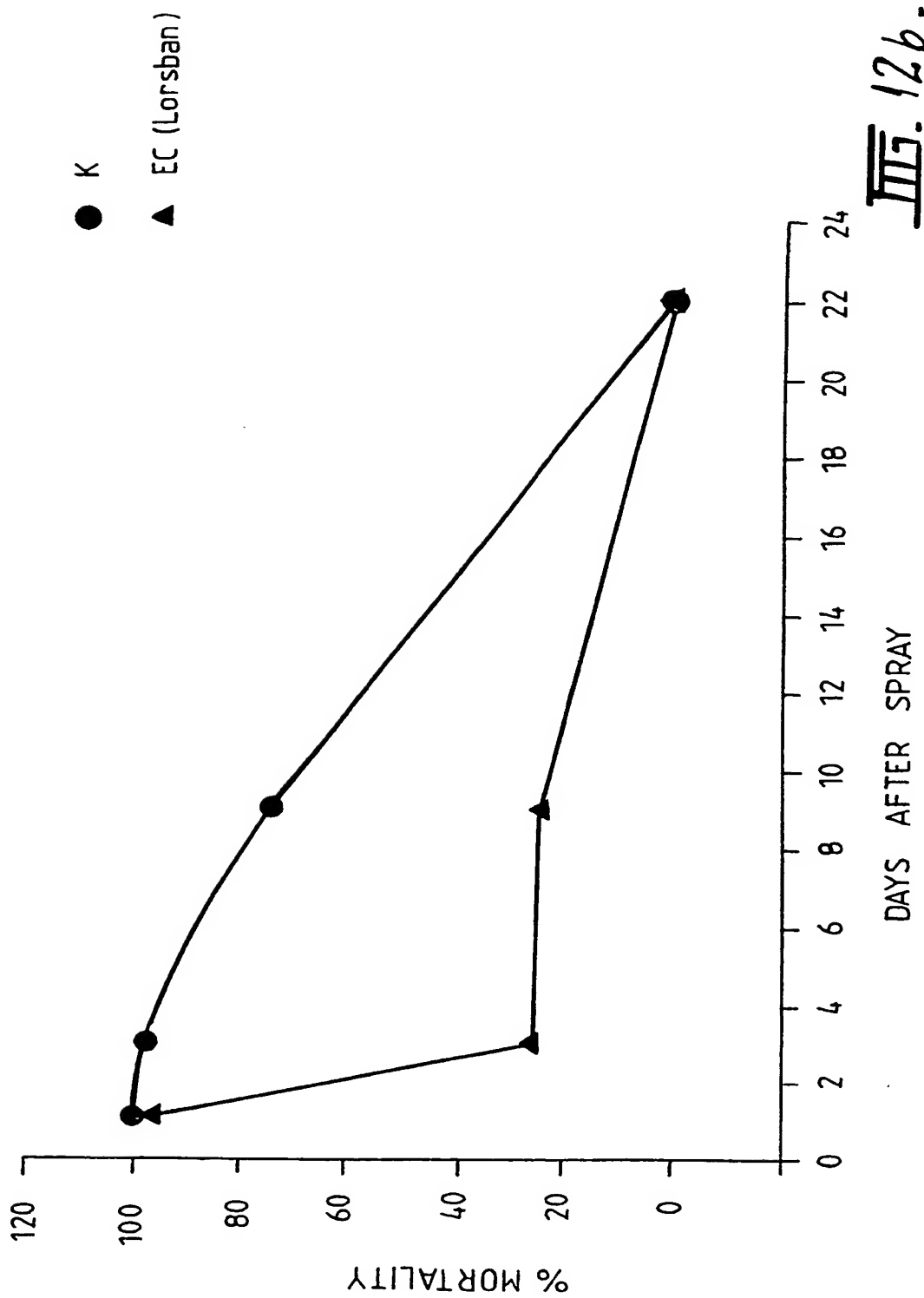


Fig. 11.

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# INTERNATIONAL SEARCH REPORT

International Application No. PCT/AU 91/00218

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) 6

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl.<sup>5</sup> A01N 25/04, 33/18, 37/22, 57/16

## II. FIELDS SEARCHED

Minimum Documentation Searched 7

Classification System	Classification Symbols
IPC	A01N 25/02, 25/04, 25/24, 17/10 CHEMICAL ABSTRACTS - KEYWORDS : VISCOUS OIL, HERBICIDE, INSECTICIDE, FUNGICIDE, NEMATOCIDE, BIOCIDES
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched 8	
AU Search : A01N 25/02, 25/04, 25/24 AU CLASSES 87.1853, 87.1855, 87.1856	

## III. DOCUMENTS CONSIDERED TO BE RELEVANT 9

Category*	Citation of Document, with indication, where appropriate, of the relevant passages 12	Relevant to Claim No 13
X	US,A, 3636207 (R.J. BOUVET and J.G. DAENINCKX) 18 January 1972 (18.01.72) See page 1 lines 52-62, page 2 lines 5-10,53-56,62-65	(1-4,12)
X	EP,A2, 0021477 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPLJ B.V.) 7 January 1981 (07.01.81) See pages 1-3,5	(1-4,11,12)
Y	AU,B, 59143/80 (540612) (SHELL INTERNATIONALE RESEARCH MAATSCHAPPLJ B.V.) 18 December 1980 (18.12.80) See pages 1-5	(1-4,5,11,12)
Y	Patents Abstracts of Japan, C 77, page 136, JP,A, 52-7437 (NIPPON SEKIYU KAGAKU K.K.) 20 January 1977 (20.01.77)	(1-4,11,12)
Y	Patents Abstracts of Japan, C 203, page 127, JP,A, 58-172304 (NIPPON NOYAKU K.K.) 10 November 1983 (10.11.83)	(1-4,5,12)
(continued)		

\* Special categories of cited documents: 10

"T"

later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"X"

document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"Y"

document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"&"

document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

13 September 1991 (13.09.91)

Date of Mailing of this International Search Report

17 September 91

International Searching Authority

Signature of Authorized Officer

Australian Patent Office

J.H. CHAN

## FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

Y	AJ,A, 40335/68 (NATIONAL RESEARCH DEVELOPMENT CORPORATION) 15 January 1970 (15.01.70) See pages 2-5	(1-4,5,12)
Y	Chemical Abstracts, Volume 98, no 11 issued 1983 March 14 (Columbus, Ohio, U.S.A.) S.A. De Licastro et al "The relation between viscosity and penetration of some diethyl p-substituted phenyl phosphorothionates and oil carriers into the cuticle of Triatoma infestans" see page 183 column 2 abstract no 84832g Pestic. Biochem. Physiol. 1983 19(1) 53-9	(1-4,12)

## V. [ ] OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE 1

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

- 1.[ ] Claim numbers ..., because they relate to subject matter not required to be searched by this Authority, namely:
- 2.[ ] Claim numbers , because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
- 3.[ ] Claim numbers ..., because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4 (a):

## VI. [ ] OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING 2

This International Searching Authority found multiple inventions in this international application as follows:

- 1.[ ] As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
- 2.[ ] As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
- 3.[ ] No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. [ ] As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

## Remark on Protest

- [ ] The additional search fees were accompanied by applicant's protest.
- [ ] No protest accompanied the payment of additional search fees.



ANNEX TO THE INTERNATIONAL SEARCH REPORT ON  
INTERNATIONAL APPLICATION NO. PCT/AU 91/00218

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Members			
US	3636207	BE 743274 GB 1288425	DE 1963583 NL 6919118	FR	1598593
EP	21477	AU 59143/80	BR 8003561	ZA	8003435
AU	59143/80	BR 8003561	EP 21477	ZA	8003435
AU	40335/68	BE 718199 FR 1603602 NL 6810301	DE 1792067 GB 1235667	ES LU	356274 56490

END OF ANNEX

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